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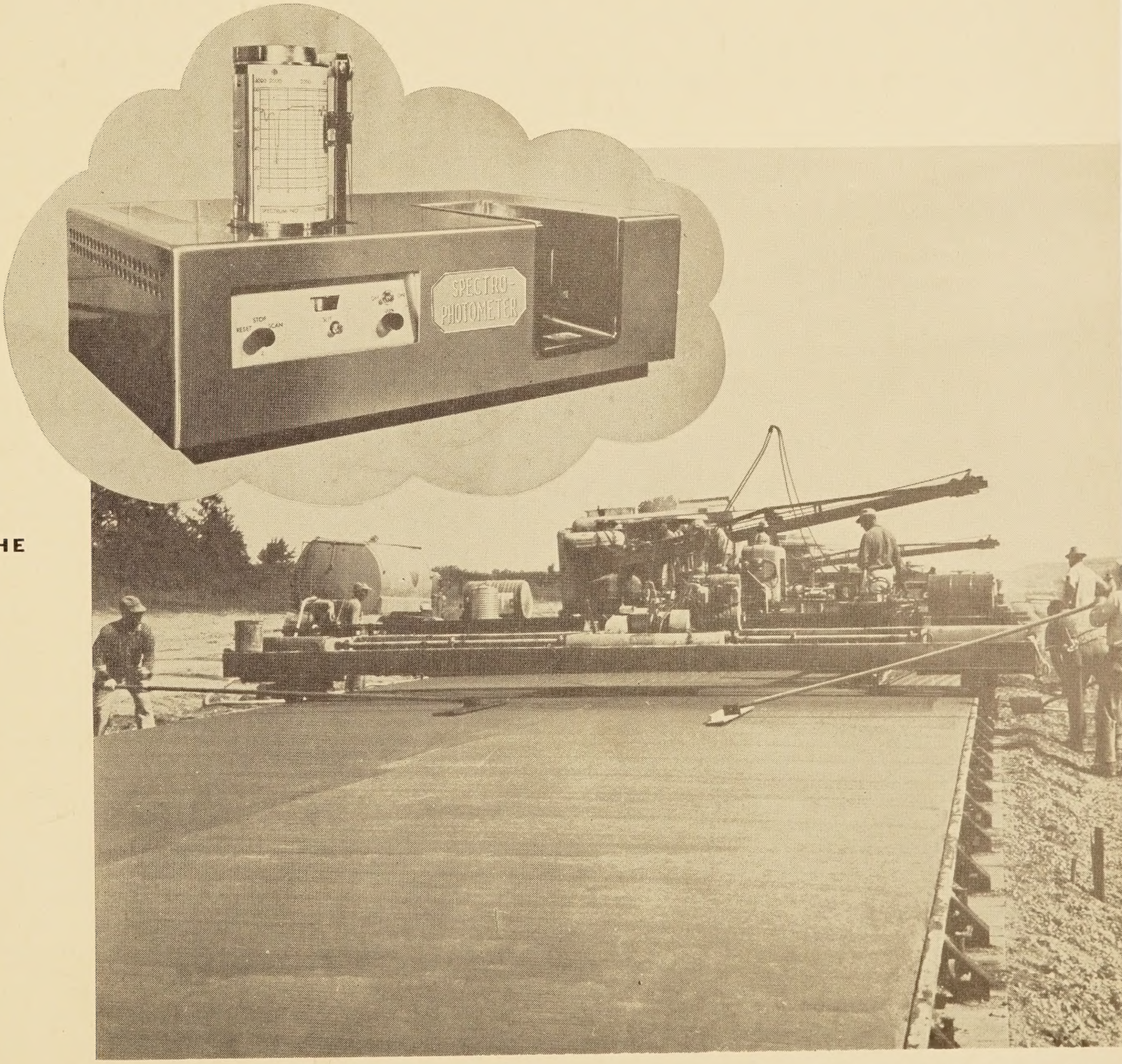

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LUTHER H. HODGES, Secretary
BUREAU OF PUBLIC ROADS
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A Symposium on Water-Reducing Retarders for Concrete

Within the past several years, admixtures to reduce water content and to retard set in portland cement concrete have come into prominent use in construction. With the recognition of benefits derived from and the increase in availability of commercial concrete retarders, the need for a specification for the acceptance and performance of all types of retarders has become great. Problems of acceptance and performance, however, confront the engineer, who is responsible for the selection and use of a satisfactory retarder, because of a lack of standard methods of testing retarders. It was believed that these problems would be greatly reduced by procedures for testing which would allow the engineer to make tests of the retarder to determine if it is acceptable and is uniform from batch-to-batch.

In an attempt to standardize testing methods for retarding admixtures, the Bureau of Public Roads in 1957 undertook an extensive investigation of the effects of commercial retarders on certain properties of portland cement concrete. A questionnaire was sent to all marketers of retarders known to the Bureau of Public Roads with a request for samples and information. Of the samples received, 25 samples from 11 companies were chosen for testing. The other samples were considered not to meet the Bureau's conditions for inclusion in the testing program because they were either not essentially retarders or were not available commercially at the time of receipt.

The study of commercial retarders was conducted in two phases. First, chemical, ultraviolet, and infrared spectral analyses were made to determine the composition of each retarder. Second, a study was made of the performance of the retarders when used in concrete. The results of the two phases of investigation are included in this issue. Also included is a recommended specification for water-reducing retarders.

All materials were analyzed for specific physical properties and chemical composition. One objective of the chemical and other analyses was to develop procedures by which such materials could be identified quickly to provide a basis for obtaining the necessary assurance that the composition of a product is uniform from batch-to-batch. Another objective of the analyses was to establish the chemical composition of typical commercial products to show possible relationships between chemical composition and the performance of concrete prepared with the retarders.

The term "retarder" is used for brevity in this issue to mean a water-reducing retarding admixture. The retarders studied were classified, according to their chemical constituents, into three general chemical types. For the purposes of discussion they are referred to as lignosulfonates (salts of lignosulfonic acid), organic acids (organic acids of the hydroxylated carboxylic type or their salts), and carbohydrates (reducing and nonreducing sugars and starches).

Water-Reducing Retarders for Concrete—Chemical and Spectral Analyses (p. 126) *deals with the results obtained by the various analyses of the retarders and the relative merits of each method in characterizing the composition of the admixtures. Specific conclusions based on the data are:*

1. Infrared spectral analysis offers the most promising means available for rapid identification and classification of retarders. This technique can be used to identify a material by obtaining a recorded spectral curve for each retarder. Less than 30 minutes is required for the analysis whereas a week is required by conventional methods of chemical analysis.

2. For specific construction projects, infrared analysis can be used to assure the purchaser of the uniformity of the admixture.

3. All three types of retarders could be distinguished from each other on the basis of infrared spectra. Although the lignosulfonate retarders had the same general infrared spectrum regardless of the type of salt present or the source of supply, in many instances, specific commercial lignosulfonates could be identified or differentiated by spectral differences caused by the manufacturing process or the presence of other ingredients. As to organic acids and carbohydrates, specific trade products could be distinguished from each other.

4. Ultraviolet spectra can also be used to identify lignosulfonate retarders and to obtain quantitative information as to their concentration. However, the spectra obtained are not as specific as are the infrared spectra.

5. Although useful in identifying retarder materials, conventional chemical analyses are time consuming and tedious and in many cases yield doubtful results. This was found to be especially true for the lignosulfonate and organic acid retarders.

Water-Reducing Retarders for Concrete—Physical Tests (p. 136) *reports the data of the effects of commercial retarders on certain properties of portland cement concrete. The tests reported therein cover time of retardation, reduction of water, durability, and compressive and flexural strengths at various ages. The conclusions given below apply to concrete prepared with the cement and aggregates in the stated proportions and conditions of mixing, molding, curing, and testing used in this investigation.*

1. To retard the setting time of concrete $2^1/_2$ to 3 hours, more retarder was required in some cases than that recommended by the manufacturer. This may have been due to the cement used in these tests, and indicates that acceptance tests of retarders should be made with the cement to be used in the proposed construction.

2. All retarders permitted some reduction in the amount of water required to prepare concrete with a specific consistency. This reduction was over 5 percent for 23 of the 25 retarders tested.

3. The use of retarders improved the compressive strength of concrete when the air content was less than 8 percent. This applied to concrete having either the same cement content or the same water content as was used in concrete prepared without a retarder.

4. The flexural strength of concrete in general was not reduced by the use of retarders if the air content was less than 8 percent. When the cement content of the concrete containing the retarder was the same as that for concrete without a retarder, use of the retarder generally furnished higher flexural strength at both 7 and 28 days. When the two concretes had the same water content, those containing the retarder generally had higher flexural strength at 7 days and about the same strength at 28 days.

5. As determined by freezing and thawing tests in the laboratory, the durability of concrete containing the retarder was in most cases less than that for concrete prepared without the retarder. However, the decrease in relative durability was significant in the case of only one retarder.

6. The contraction of concrete during continuous storage in laboratory air or the expansion during continuous moist storage was about the same for concrete prepared with or without a retarder.

7. An overdose of four times the normal amount of retarder generally caused a long delay in the hardening of the concrete. However, if the air content of this concrete was not over 8 percent, the compressive strength at an age of 28 days was usually greater than that of the concrete prepared without a retarder.

8. More retarder was usually required to retard the setting of concrete at a temperature of 90° F. than at 73° F. With few exceptions, the compressive strength of concrete prepared with a retarder at 90° F. was greater than that prepared at the same temperature without a retarder.

The data obtained from the study of the effects of retarders on concrete were used to prepare a specification for the acceptance and use of these retarders. The recommended specification is given on page 153. It is of interest to note that of the 25 retarders used in the test, 16 retarders met all of the requirements of the proposed specifications.

Water-Reducing Retarders for Concrete—Chemical and Spectral Analyses

BY THE DIVISION OF PHYSICAL RESEARCH
BUREAU OF PUBLIC ROADS

Reported[1] by WOODROW J. HALSTEAD,
Supervisory Chemist, and
BERNARD CHAIKEN, Chemist[2]

IN THE PAST SEVERAL YEARS, admixtures to reduce water content and retard set in portland cement concrete have come into prominent use in construction. These materials are usually complex organic products which are sold under various trade names. As yet there are no standard specifications or methods for testing retarders, but the American Society for Testing Materials (ASTM) is now considering these specifications and methods for testing such admixtures. These include among other items, requirements for the effects of water-reducing retarders on the compressive strength of the concrete, resistance to freezing and thawing, and change in volume. These tests may require a period of one year or more for completion and consequently are intended for the primary evaluation of such admixtures.

After an admixture has been found acceptable under these specifications, subsequent purchases of the same material for use on specific projects may not be subjected to extensive testing because of the time and cost involved. Consequently, the presently proposed specifications for retarding and water-reducing admixtures suggest that the purchaser obtain assurance that the admixture supplied for use on each field job or project be equivalent in composition to the original or reference admixture subjected to the exhaustive tests required by the specifications. To explore the best means of doing this, chemical analyses, as well as ultraviolet and infrared spectral analyses, were made on 25 commercial or trade-name retarders. All materials were analyzed for specific properties and chemical composition.

Types of Retarders Studied

The retarders investigated were found to be of three general chemical types: lignosulfonates; salts of organic hydroxy-carboxylic acids; and carbohydrates. A general discussion of the origin and characteristics of these major types of retarders studied is given below.

Lignosulfonates

With one exception, the lignosulfonate materials studied were derived from spent sulfite liquor obtained in the acid process of wood pulping. The single exception was derived from the Kraft (alkaline) process. Materials were supplied as the calcium, sodium, or ammonium salts, and either as a powder or in a water solution.

Lignosulfonates are considered to be polymers of high molecular weight. A single sample may contain molecules ranging in molecular weight from several hundred to 100,000 with an average molecular weight of approximately 10,000 (*1*, *2*).[3] Structurally, these materials are polymers of a substituted phenyl propane grouping. The repeating monomer unit has been represented as shown in figure 1, diagram A (*2*). The functional units of interest are hydroxyl (OH), methoxyl (OCH_3), phenyl ring, and the sulfonic group (SO_3H). In the lignosulfonate salts, a metal or ammonium cation replaces the hydrogen in the sulfonic grouping.

Many commercial lignosulfonates also contain varying amounts of reducing sugars. A typical analysis showed the following percentages of wood sugars based on total sugar content (*3*): mannose—48 percent; glucose—15 percent; xylose—15 percent; galactose—10 percent; arabinose—6 percent; fructose—under 2 percent; and sugars unaccounted for—4 percent. Much of these sugars can be removed by suitable processing techniques.

Organic hydroxy-carboxylic acids

Salts and complexes of organic hydroxy-carboxylic acids, sometimes referred to as sugar acids, are derived from the fermentation or oxidation of carbohydrates, such as dextrose, glucose, or starch. They are characterized by several hydroxyl groups and either one or two terminal carboxylic acid (COOH) groups attached to a relatively short carbon chain as illustrated in diagram B of figure 1. As retarders, they are generally supplied as metal salts in which the hydrogen in the carboxylic acid group is replaced by sodium, potassium, etc.

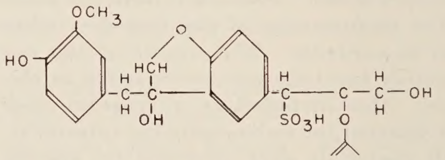
Carbohydrates

Carbohydrates, such as reducing sugars (e.g., glucose), have been used as retarders (*4*). However, non-reducing sugars, sucrose or cane sugar, are more illustrative of the type of carbohydrate evaluated in this study. The structure of sucrose is shown in diagram C of figure 1. Here again, hydroxyl groups are characteristic of the material.

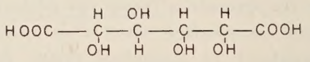
Physical Properties

The physical properties of each retarder evaluated in this study are shown in table 1. Most of the materials were powders, the rest were aqueous solutions. The color code was obtained by a visual comparison with the closest color standard available in Federal Standard No. 595. Although this Federal Standard is intended primarily for paints, it is useful for describing colors of other materials by standardized code number.

The specific gravities of the liquid samples were determined with a hydrometer. Values for pH were obtained electrometrically on liquid samples as received, and on aqueous solutions containing one percent of the solid materials. Rather low pH values, indicating significant acidity, were obtained on a complexed hydroxy-carboxylic acid retarder (No. 6) and all the ammonium lignosulfonates (Nos. 7, 10, and 17). Several calcium

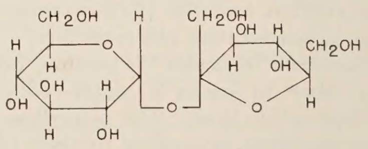


A. STRUCTURAL UNIT OF LIGNOSULFONIC ACID



$$HOOC-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-COOH$$

B. HYDROXY-CARBOXYLIC ACID



C. CARBOHYDRATE (SUCROSE)

Figure 1.—Typical chemical structures of retarders studied.

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[1] Presented at the 40th Annual Meeting of the Highway Research Board, Washington, D.C., January 1961.

[2] Acknowledgment is made to Raymond Cherwinski and L. B. Hayes, Analytical Chemists, for their assistance in carrying out the chemical and ultraviolet analyses.

[3] Italic numbers in parentheses refer to a list of references on page 135.

Table 1.—Physical properties of retarders

Retarder No.	Form	Color		Odor	Specific gravity, 77° F./77° F.[2]	pH[3]	Solubility in—[4]			Foaming properties, milliliters of foam after—[5]				Unusual characteristics of 1-percent aqueous solution
		Observed	Code[1]				Water	Alcohol benzene chloroform	Dimethyl sulfoxide	1 minute	2 minutes	5 minutes	15 minutes	
1	Liquid	None	------	Phenolic	1.143	7.4	----	--------	------	0	0	0	0	
2	Solid	White	37778	Woody	--------	7.8	I	I	I	0	0	0	0	
3	do	Olive	30118	do	--------	7.2	S	I	I	10	5	3.5	1	
4	Liquid	Amber[6]	[6] 23655	Rancid	1.182	6.8	----	--------	------	0	0	0	0	U. V. fluorescence.
5	do	Wine	20109	Pungent	1.148	7.1	----	--------	------	0	0	0	0	
6	do	Amber	33538	None	1.178	2.8	----	--------	------	0	0	0	0	
7	Solid	Brown	10091	Woody	--------	3.3	PS	I	I	10	7	4	1.5	Mold growth.
8	do	Pink	30313	None	--------	7.6	I	I	I	0	0	0	0	
9	Liquid	Dark brown	10032	Rancid	1.196	8.2	----	--------	------	0	0	0	0	
10	Solid	Medium brown	10091	Woody	--------	3.2	S	I	I	2	2	1.5	1	Mold growth.
11	do	Light brown	20400	do	--------	6.8	S	I	I	4	2	0	0	Do.
12	do	Mustard	30266	do	--------	6.7	S	I	PS	0	0	0	0	
13	do	Medium brown	30117	do	--------	9.4	PS	I	I	1	.5	0	0	
14	do	Tan	31643	do	--------	4.6	S	I	I	5	4	3	1.5	
15	do	Olive	30009	do	--------	7.4	S	I	I	11	8	4.5	2	
16	do	Tan	31643	do	--------	7.3	PS	I	PS	9	6	2.5	1	
17	do	Light brown	20400	do	--------	3.8	S	I	S	1.5	1	.5	0	Mold growth.
18	do	Tan	31643	do	--------	7.4	S	I	I	3.5	2	1	.5	
19	do	Light brown	20400	do	--------	6.6	S	I	I	.5	0	0	0	
20	Liquid	Dark brown	10032	do	1.155	4.8	----	--------	------	12	8	4	1	
21	do	do	10032	do	1.147	4.7	----	--------	------	10	7	3	.5	
22	Solid	Dark brown	30045	do	--------	8.8	S	I	I	5	2.5	1	.5	
23	do	Medium brown	10091	do	--------	9.5	S	I	I	0	0	0	0	
24	do	Tan	31643	do	--------	7.8	PS	I	I	1	1	.5	0	
25	do	do	31643	do	--------	4.6	PS	I	I	7	7	7	7	

[1] Federal Standard No. 595 (by visual matching).

[2] Hydrometer method on liquid samples as received.

[3] Electrometric method on liquid samples as received, and on solid samples in 1-percent water solution.

[4] At room temperature: I=insoluble (less than 0.01 g. in 10 ml.); PS=partially soluble (between 0.01 and 1 g. in 10 ml.); S=soluble (more than 1 g. in 10 ml.).

[5] 20 ml. of 1-percent aqueous solution in 50 ml. stoppered graduate. Inverted 30 times. Readings then noted at indicated time intervals. (Modified from McCutcheon, J. W., *Synthetic Detergents*, 1950, p. 79.)

[6] By transmitted light. By reflected light, color had a greenish fluorescence (equivalent to Code 14187).

lignosulfonates (Nos. 14, 20, 21, and 25) had moderately low pH values, possibly as a result of incomplete neutralization of the sulfonic acid groups during processing.

The apparent insolubility of samples Nos. 2 and 8 in water was caused by the large amount of inert filler in each material. Ultraviolet fluorescence was observed on a 1-percent aqueous solution of sample No. 4, most likely because of a fluorescent dye used by the producer to characterize his product. As noted in table 1, a mold growth developed in several of the 1-percent aqueous solutions after standing for about one week. Only retarder No. 25 produced a lasting foam in the foaming test. This was apparently a result of some synthetic detergent which has been incorporated into the admixture.

Qualitative Chemical Test Results

Table 2 shows the results of qualitative chemical tests used to identify and classify each material for further evaluation. References to the methods used are given in the footnotes to the

Table 2.—Qualitative tests on retarders[1]

Retarder No. (1)	Sulfonated organics (Basic fuchsin test)[2]			Lignosulfonate (Proctor-Hirst test)[3] (5)	Chloride (AgNO$_3$ test) (6)	Sulfate (BaCl$_2$ test) (7)	Carbonate (acid effervescence) (8)	Calcium (oxalate test) (9)	Sodium (flame phot.) (10)	Potassium (flame phot.) (11)	Nitrogen		Hydroxy acids (dinaphthol test)[5] (14)	Complexing agents (CuSO$_4$+NaOH test)[6] (15)	Melting point of phenylhydrazine derivative, °C.[6] (16)
	Original material (2)	Alcohol-insoluble fraction (3)	Alcohol-soluble fraction (4)								Ammoniacal[4] (12)	Albuminoid[4] (13)			
1[7][8]	N	-----	-----	N	N	N	N	N	T	N	-----	-----	----------	P (light blue)	
2	P	P	N	T	N	N	P	N	T	N	N	N	----------	----------	No derivative.
3	P	P	N	P	N	Q	N	P	P	T	N	N	----------	----------	
4	N	-----	-----	N	N	N	N	N	P	T	-----	-----	P (green)	P (light blue)	188 to 189.
5[9]	N	-----	-----	N	P	N	N	N	T	T	N	P	P (blue-green)	P (medium blue)	189 to 191.
6[10]	N	-----	-----	N	N	N	N	N	T	N	-----	-----	----------	P (light blue)	No derivative.
7	P	P	N	P	N	Q	N	N	T	T	P	P	----------	----------	
8	N	-----	-----	N	N	N	N	P	P	T	-----	-----	P (light green)	P (light blue)	No derivative.
9	N	-----	-----	N	P	N	N	N	P	P	-----	-----	P (green)	P (blue-green)	180 to 182.
10	P	P	N	P	N	Q	N	N	T	T	P	P	----------	----------	
11	P	P	N	P	P	P	N	P	P	P	N	N	----------	----------	
12	P	P	N	P	N	N	N	P	P	T	N	N	----------	----------	
13	P	P	N	P	N	N	P	T	P	T	N	N	----------	----------	
14	P	P	N	P	N	P	N	P	P	T	N	N	----------	----------	
15	P	P	N	P	N	P	N	N	P	T	N	N	----------	----------	
16	P	P	N	P	N	P	N	P	P	T	N	N	----------	----------	
17	P	P	N	P	N	Q	N	N	T	T	P	P	----------	----------	
18[11]	P	P	N	P	N	N	N	P	P	T	N	N	----------	P (light green)	No derivative.
19	P	P	N	P	N	Q	N	N	P	P	N	N	----------	----------	
20	P	P	N	P	N	N	N	P	T	T	N	N	----------	N	
21	P	P	N	P	N	N	N	P	T	T	N	N	----------	N	
22	P	P	N	P	N	Q	N	N	P	N	N	N	----------	----------	
23	P	P	N	P	N	Q	N	N	P	T	P	P	----------	----------	
24	P	P	N	P	P	T	N	P	P	P	P	P	----------	----------	
25	P	P	P	P	N	P	N	P	P	T	N	N	----------	----------	

[1] Code: P=positive indication; N=negative indication; T=trace indicated; Q=questionable indication.

[2] Modified from Wallin, Anal. Chem., vol. 22, 1950, pp. 616–7.

[3] Jour. ALCA, vol. 51, No. 7, 1956, pp. 353–76.

[4] PUBLIC ROADS, vol. 27, No. 12, 1954, p. 268.

[5] F. Feigl, Qualitative Analysis by Spot Tests, 3d ed., 1946.

[6] Test procedure given in text.

[7] A positive indication of phenols was obtained by the Millon test (Feigl, Qualitative Analysis by Spot Tests, 3d ed., 1946, p. 330).

[8] A positive indication of sucrose was obtained by the alpha-naphthol test (Griffin, R. C., Technical Methods of Analysis, 2d ed., 1927, p. 567).

[9] A positive indication of triethanolamine was obtained by the Kraut test (*Official Methods of Analysis*, A.O.A.C., 7th ed. 1950, p. 609).

[10] Positive indications of zinc (sulfide test), and boron (flame and turmeric tests) were obtained.

[11] A negative test for triethanolamine was obtained by means of the Kraut test (see footnote 9).

table. Positive test results are shown by "P", negative results by "N", trace quantities by "T", and questionable results by "Q".

Sulfonated organic material was identified with basic fuchsin. This reagent reacts with sulfonates in acid solution to form a magenta-colored complex which can be extracted with chloroform. The results are given in column 2. The method has been described as a quantitative spectrophotometric determination of sulfonated and sulfated organic materials (*5*). When a positive result was obtained on the original material, additional tests were made on the alcohol-insoluble and alcohol-soluble fractions of the retarder. A positive result on the alcohol-insoluble fraction suggests the presence of lignosulfonates, since lignosulfonates are insoluble in alcohol. A positive test result on the alcohol-soluble fraction, as for retarder No. 25, suggests the presence of a sulfonated or sulfated synthetic detergent. Consequently, the result on sample No. 25 reinforces the findings of the foaming test, that this material contained a synthetic detergent.

A more specific indication of lignosulfonate is given by the Proctor-Hirst test. In this test, an acidified clear extract is treated with aniline. A resultant cloudiness is indicative of lignosulfonate. The test is considered to be quite reliable (*6*). In every case, these results are in agreement with the findings from the basic fuchsin test.

Columns 6 through 11 in table 2 show the the results of tests for chloride, sulfate, carbonate, calcium, sodium, and potassium using standard procedures. Positive test results for chloride and sulfate are not entirely reliable in the presence of some organics, such as were found in some retarders, because of the possible precipitation of organic salts in the presence of silver and barium reagents.

Test results for both ammoniacal and albuminoid nitrogen are shown in columns 12 and 13. In the test for ammoniacal nitrogen, an alkaline solution of the sample was boiled and the vapor tested with red litmus paper for volatile ammonia. A blue color indicated the presence of an ammonium salt. Following the removal of volatile ammonia, permanganate was added and the test repeated to detect albuminoid nitrogen. Positive results suggest the presence of amines and similar nitrogenous compounds.

Zinc was detected in sample No. 6 by precipitation as a white sulfide, and boron by flame tests and turmeric paper. In sample No. 1, a phenolic odor was detected which was attributed to a phenol-type material. This phenolic material was confirmed by the Millon test. This material probably serves as a fungicide. The same retarder also gave a positive test result for sucrose. However, substances similar to sucrose may give positive results with alpha-naphthol reagent, so that these results were not conclusive.

The results of the dinaphthol test which has been used to identify many hydroxy-carboxylic acids are shown in column 14. Acids such as tartaric, malic, tartronic, glucoronic, and gluconic reportedly give a green fluorescence (*7*). Where a positive test result was obtained, the nature of the color which developed is shown in parentheses.

Test results for complexing agents are shown in column 15. Although not specific, the test may be used to detect such complexing agents as triethanolamine, sugars, hydroxy-carboxylic acids, etc.[4] Where positive results are shown, the color of the copper complex formed is also given.

A specific check for triethanolamine was made by means of the Kraut test. Sample No. 5 gave a positive indication of the presence of this compound, while sample No. 18 gave a negative test for triethanolamine.

Column 16 shows the melting points of phenylhydrazine derivatives of several retarders. Ordinarily, such derivatives are obtained with carboxylic acids, and the melting points of these derivatives have been used for qualitative analyses.[5] This test was suggested by one producer of retarders; however, in this study it was found that duplicate determinations failed to give reasonably reproducible results.

On the basis of the above qualitative tests, the following summarization was possible. Retarder No. 1 contained a sugar and a phenolic additive. Five samples were found to be the following derivatives of hydroxy-carboxylic acids: Nos. 4, 8, and 9 appeared to be metal salts; No. 6 a zinc borate complex; and No. 5 a triethanolamine salt. The other materials were lignosulfonate salts of various types.

Quantitative Chemical Analyses

Inorganic constituents

Table 3 gives the results of the analyses for inorganic constituents in each retarder sample. Moisture or water was determined by oven loss at 105° C. except for sample No. 5. This material had a tendency to decompose or volatilize at that temperature, and therefore its moisture content was determined by heating at 50° C. under vacuum.

Total ash content was determined by ignition at 600° C., and HCl insoluble by treating the ash with hydrochloric acid (1:5). The acid-soluble ash constituents were then determined by conventional methods of analysis and reported as the oxides. The alkalies, Na_2O and K_2O, were determined by flame photometry, and zinc by ferrocyanide titration with an external indicator. Carbon dioxide was determined by wet evolution with hydrochloric acid and chlorides by the Mohr titration. Boron was analyzed by distillation with methyl alcohol followed by titration using an ASTM standard procedure. Total sulfur was obtained by wet oxidation followed by precipitation as barium sulfate.

Summary of inorganic results

Retarders Nos. 1, 5, 7, 10, and 17 appeared to be composed almost exclusively of organic material that was completely volatilized at 600° C. Retarder No. 2 contained limestone or dolomitic limestone along with zinc, perhaps as zinc oxide. Samples Nos. 4 and 9 were composed of sodium and potassium salts, respectively, of carboxylic acids. Sample No. 6 contained zinc and boron, most likely in the oxide form. Retarder No. 8 contained a large amount of insoluble siliceous material and iron oxide. Retarders Nos. 11 and 24 contained calcium chloride and No. 13 contained a substantial amount of sodium carbonate.

Organic constituents

The organic constituents determined in each retarder are shown in table 4. References to the methods used are given in the footnotes. The volatile matter at 600° C. is an approximate measure of total organic material present. Methoxyl was determined by the Zeisel method.

Lignosulfonates were determined by a recommended cinchonine procedure. It appears from the results shown, as well as the results of duplicate determinations, that the cinchonine procedure yielded erratic results. Lignin content was also calculated from the methoxyl values as given by the Technical Association of the Pulp and Paper Industry (TAPPI method T629, m-53). While this procedure was empirical, the results appeared to be more realistic than those obtained by the cinchonine method.

A colorimetric procedure was used to determine total carbohydrates by the anthrone method (*8*), and reducing sugars were determined by the Somogyi-iodometric method, after precipitation of non-carbohydrates with basic lead acetate. In both cases the constituent was calculated as glucose.

Sucrose was determined by the AOAC (Association of Official Agricultural Chemists) official chemical procedure by direct weighing of cuprous oxide. The anionic sulfonated detergent was determined colorimetrically with basic fuchsin after first extracting the detergent with alcohol. The method used was similar to that prescribed by Wallin (*5*) except that visual estimation was made in Nessler tubes because of the staining effect by the reagent on spectrophotometric cells.

Phenol was determined from the spectrophotometric absorption at 270 millimicrons, using a calibration curve of known concentrations of phenol plotted against absorbance.

Total nitrogen was obtained by the Kjeldahl distillation procedure, and ammoniacal nitrogen was determined by distillation from an alkaline solution. After removing ammoniacal nitrogen, permanganate was added and albuminoid nitrogen obtained by distillation. Fixed nitrogen was calculated by difference.

Classification and probable composition

Based on the results of chemical analysis, the classification and probable composition of each retarder are given in table 5. The majority of the retarders analyzed were found to be ammonium, sodium, or calcium salts of lignosulfonic acid. The approximate amount of lignosulfonate salt shown was obtained by empirical calculations based on methoxyl values. In two samples, Nos. 3 and 15, the empirical calculation gave unreasonably high results because of high methoxyl contents. Consequently, the values shown for these samples were obtained by difference and therefore represented the maximum amounts of lignosulfonate possible. Carbohydrates, both nonreducing and reducing-sugar types, were calculated as glucose.

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[4] Details of the test procedure are as follows: To 10 ml. of a 1-percent solution of the admixture, add 1 ml. of 10-percent NaOH, mix, and add 1 ml. of 3-percent $CuSO_4$. Mix and note whether a soluble colored copper complex is formed.

[5] Details of the test procedure are as follows: To a test tube (35 ml., 20 x 150 mm.) add 1 ml. of a 50-percent aqueous solution of active ingredient, add 4 ml. H_2O, 0.7 ml. of glacial acetic acid and 1.0 ml. phenyl hydrazine. Fit with reflux tube approximately 8 inches long, heat in boiling water and reflux 3 hours. Filter while hot, collect filtrate, cool and let crystallize from 2 hours to overnight. Collect crystals by filtration, wash with 5 ml. cold water, then 5 ml. alcohol. Dry at room temperature and determine melting point.

Only one lignosulfonate retarder, No. 25, was found to contain a sulfonated synthetic detergent, which was possibly a sodium alkyl aryl sulfonate. Two of the lignosulfonates, Nos. 11 and 24, contained substantial amounts of calcium chloride (9.8 and 25 percent, respectively). Retarder No. 2 contained 80–90 percent of dolomitic limestone and about 7 percent zinc oxide. Retarder No. 13 contained approximately 29 percent sodium carbonate.

The derivatives of hydroxy-carboxylic acids were found to be metallic salts—sodium, calcium, and potassium; triethanolamine salt; and zinc borate complex. These materials contained little or no carbohydrates. Retarder No. 8, a solid material, contained iron oxide and siliceous filler. The organic carboxylic material in each retarder was estimated by difference.

Only one retarder, No. 1, was found to be a carbohydrate. This was essentially a nonreducing sugar (sucrose). It contained some phenol to prevent fermentation or mold growth.

It is quite possible that these retarders may contain minor amounts of other organic substances not discussed here, but no effort was made in this study to identify all such minor constituents.

Table 3.—Inorganic constituents in retarders, by percent of constituent

Retarder No.	Moisture or water, at 105° C.[1]	Analyses on dry solids basis[2]													
		Total ash at 600° C.	HCl (1:5) Insoluble	SiO_2	R_2O_3 [3]	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	ZnO[4]	CO_2, wet evolution method	Chloride as $CaCl_2$	B_2O_3 [5]	Total sulfur, as SO_3 [6]
1	66.7	0.2	------	------	------	------	------	------	------	------	------	------	------	------	------	------
2	.4	97.2	5.6	Neg.	0.8	------	34.3	5.1	Neg.	Neg.	0.9	6.7	37.8	------	------	0.6
3	6.8	17.7	.1	0.2	.4	------	3.2	1.0	5.2	0.1	6.3	------	------	0.0	------	9.8
4	68.2	24.8	Neg.	Neg.	Neg.	------	Neg.	Neg.	12.6	.2	Neg.	------	------	------	------	------
5	[7] 57.1	.4	------	------	------	------	------	------	------	------	------	------	------	------	------	.0
6	72.5	32.5	Neg.	Neg.	------	------	------	------	Neg.	Neg.	Neg.	15.6	------	------	11.9	------
7	4.5	1.3	.1	Neg.	Neg.	------	.3	.2	.4	.2	Neg.	------	------	------	------	14.3
8	.7	90.0	[8] 67.5	2.2	14.0	6.7	5.2	2.0	.9	.1	Neg.	------	------	------	------	------
9	66.5	32.4	Neg.	.8	4.0	------	Neg.	Neg.	.5	16.5	Neg.	------	------	------	------	------
10	5.1	.7	Neg.	.2	.1	------	Neg.	Neg.	Neg.	Neg.	Neg.	------	------	------	------	14.0
11	6.2	28.2	.6	Neg.	Neg.	------	11.4	.2	2.1	.3	6.7	------	------	9.8	------	13.2
12	4.4	21.2	.2	Neg.	.2	------	10.8	.7	.2	.2	6.0	------	------	.0	------	11.4
13	8.8	47.0	.2	.1	.6	------	3.1	.6	16.3	.1	10.1	------	12.6	------	------	9.6
14	6.5	15.2	.1	Neg.	.1	------	4.6	.4	.1	.3	3.3	------	------	------	------	9.2
15	7.4	23.7	.3	.2	Neg.	------	.6	1.1	9.2	.1	9.0	------	------	------	------	12.0
16	5.3	16.4	.2	Neg.	Neg.	------	6.7	.5	.7	.4	7.1	------	------	.0	------	13.5
17	7.6	.8	Neg.	Neg.	Neg.	------	Neg.	Neg.	.1	.3	.2	------	------	------	------	13.5
18	7.2	9.4	.1	Neg.	.6	------	5.2	Neg.	Neg.	Neg.	3.2	------	------	------	------	11.8
19	5.4	25.4	.1	.3	.1	------	Neg.	Neg.	9.6	.1	13.6	------	------	------	------	16.9
20	69.0	22.5	Neg.	.2	Neg.	------	9.5	Neg.	Neg.	Neg.	10.8	------	------	------	------	13.1
21	70.3	22.3	Neg.	.2	Neg.	------	9.1	Neg.	Neg.	Neg.	11.9	------	------	------	------	15.6
22	8.5	45.2	.3	Neg.	.3	------	Neg.	Neg.	20.0	.1	22.2	------	------	------	------	27.2
23	7.2	34.7	.2	Neg.	Neg.	------	.6	.1	12.8	.3	10.2	------	------	------	------	7.6
24	4.0	44.8	.6	.1	Neg.	------	17.7	.3	3.2	.4	9.5	------	------	25.0	------	16.0
25	6.5	17.2	.1	Neg.	.1	------	6.9	.7	.7	.1	6.7	------	------	------	------	15.6

[1] Loss at 105° C., calculated on basis of material as received.
[2] Neg. = Negligible.
[3] Fe_2O_3 plus Al_2O_3.
[4] Volumetric determination with ferrocyanide.
[5] Distillation method, modified from method C 169–53, sec. 18; ASTM Standards Part. 3, 1955, p. 907.
[6] TAPPI, T 629–m53.
[7] Loss at 50° C., vacuum.
[8] Mainly siliceous matter.

Table 4.—Organic constituents, in percentages by weight of dry solids

Retarder No.	Volatile matter at 600° C.	Methoxyl[1]	Lignosulfonate (cinchonine method)[2]	Lignin, calculated from methoxyl[3]	Total carbohydrates, as glucose[4]	Reducing sugars, as glucose[5]	Sucrose (AOAC method)[6]	Anionic sulfonated synthetic detergent[7]	Phenol[8]	Nitrogen			
										Total (as N)[1]	Ammoniacal (as NH_3)[1]	Albuminoid (as N)[9]	Fixed (as N)[10]
1	99.8	--------	--------	--------	--------	0.0	96.3	--------	1.4	--------	--------	--------	--------
2	2.8	0.2	1.3	1.7	0.7	.6	--------	--------	--------	--------	--------	--------	--------
3	82.3	11.8	69.2	92.2	4.0	.8	--------	0.0	--------	--------	--------	--------	--------
4	75.2	--------	--------	--------	.4	.2	--------	--------	--------	--------	--------	--------	--------
5	99.6	--------	--------	--------	.9	.5	--------	--------	--------	3.9	0.1	2.0	3.8
6	67.5	--------	--------	--------	.6	.01	--------	--------	--------	--------	--------	--------	--------
7	98.7	8.2	109.6	64.2	5.9	2.9	--------	--------	--------	3.2	2.0	--------	1.7
8	10.0	--------	--------	--------	1.0	.05	--------	--------	--------	--------	--------	--------	--------
9	67.6	--------	--------	--------	.4	.1	--------	--------	--------	--------	--------	--------	--------
10	99.3	8.4	43.7	65.2	5.4	3.5	--------	--------	--------	3.4	1.4	--------	2.2
11	71.8	6.4	100.6	49.8	5.2	1.5	--------	--------	--------	--------	--------	--------	--------
12	78.8	7.2	103.8	56.2	4.7	2.7	--------	--------	--------	--------	--------	--------	--------
13	53.0	7.1	123.4	55.5	.8	.3	--------	--------	--------	--------	--------	--------	--------
14	84.8	6.6	110.2	51.9	9.1	5.1	--------	--------	--------	--------	--------	--------	--------
15	76.3	11.4	104.4	88.6	2.5	.3	--------	--------	--------	--------	--------	--------	--------
16	83.6	7.5	96.9	58.8	7.6	3.8	--------	--------	--------	--------	--------	--------	--------
17	99.2	8.2	98.1	63.9	12.2	8.1	--------	--------	--------	3.2	2.7	--------	1.1
18	90.6	6.9	114.6	53.7	8.6	3.0	--------	--------	--------	1.8	.0	.5	1.8
19	74.6	7.1	92.8	54.7	8.9	4.8	--------	--------	--------	--------	--------	--------	--------
20	77.5	6.2	93.0	48.7	5.4	1.3	--------	--------	--------	--------	--------	--------	--------
21	77.7	7.3	117.6	56.9	6.8	2.4	--------	--------	--------	--------	--------	--------	--------
22	54.8	5.4	57.5	42.3	.6	.02	--------	--------	--------	--------	--------	--------	--------
23	65.3	6.9	65.5	53.7	2.3	.3	--------	--------	--------	.9	.0	--------	.9
24	55.2	2.8	93.5	21.9	1.4	.3	--------	--------	--------	1.0	.2	.6	.8
25	82.8	8.6	103.5	67.2	10.0	4.7	--------	1.1	--------	--------	--------	--------	--------

[1] Public Roads, vol. 27, No. 12, p. 268, 1954.
[2] Jour. ALCA, vol. 51, No. 7, p. 353, 1956.
[3] TAPPI, T629-m53; methoxyl divided by 0.128.
[4] Anthrone method; Morris, Science, vol. 107, 1948, p. 254–5.
[5] Somogyi iodometric volumetric method, Jour. Biol. Chem., vol. 160, No. 1, 1945, p. 61.
[6] AOAC method 29.29.
[7] Colorimetric method (basic fuchsin), Wallin, Anal. Chem., vol. 22, 1950, p. 616.
[8] By spectrophotometric absorption at 270 millimicrons.
[9] AOAC method 2.37.
[10] Calculated from: total nitrogen − ammoniacal nitrogen.

Table 5.—Classification and probable composition of retarders, percent of constituent on dry solids basis [1]

Retarder type	Retarder No.	Water [2]	Ligno-sulfonate salt [3]	Carbohydrates [4]		Calcium chloride	Zinc oxide	Iron oxide and alumina	Organic carboxylic material [7]	Miscellaneous constituents (percent)
				Non-reducing types [5]	Reducing sugars [6]					
Lignosulfonates:										
Ammonium salts	7	4.5	76	3.0	2.9	------	------	------	--------	
	10	5.1	77	1.9	3.5	------	------	------	--------	
	17	7.6	76	4.1	8.1	------	------	------	--------	
Sodium salts	15	7.4	[9] 94	2.2	.3	------	------	------	--------	
	19	5.4	66	4.1	4.8	------	------	------	--------	
	[8] 22	8.5	51	.6	.02	------	------	------	--------	
	23	7.2	64	2.0	.3	------	------	------	--------	
Calcium salts	2	.4	2	.1	.6	------	6.7	------	--------	80–90 dolomitic limestone.
	3	6.8	[9] 93	3.2	.8	0.0	------	------	--------	0.0 synthetic detergent.
	11	6.2	59	3.7	1.5	9.8	------	------	--------	
	12	4.4	67	2.0	2.7	.0	------	------	--------	
	13	8.8	66	.5	.3	------	------	------	--------	29 sodium carbonate.
	14	6.5	62	4.0	5.1	------	------	------	--------	
	16	5.3	70	3.8	3.8	.0	------	------	--------	
	18	7.2	64	5.6	3.0	------	------	------	--------	
	20	69.0	58	4.1	1.3	------	------	------	--------	
	21	70.3	68	4.4	2.4	------	------	------	--------	
	24	4.0	26	1.1	.3	25.0	------	------	--------	
	25	6.5	80	5.3	4.7	------	15.6	------	--------	1.1 synthetic detergent.[11]
Organic acids:										
Metal salts:										
Sodium (9.3 percent Na)	4	68.2	------	.2	.2	------	------	------	90	
Calcium (3.7 percent Ca)	8	.7	------	.9	.1	------	------	14	10	71 inert siliceous matter.
Potassium (13.7 percent K)	9	66.5	------	.3	.1	------	------	------	86	
Triethanolamine salt	5	57.1	------	.5	.5	------	------	------	57	42 triethanolamine.[12]
Zinc borate complex	6	72.5	------	.6	.01	------	15.6	------	72	11.9 boric oxide (B_2O_3).
Carbohydrates:										
Sucrose	1	66.7	------	[10] 96.3	.0	------	------	------	--------	1.4 phenol.

[1] Based on results shown in tables 1–4.

[2] Based on weight of sample as received.

[3] Approximate value obtained by the following empirical calculations: Methoxyl/0.128=lignin (TAPPI, T 629 m-53); lignin×1.154=lignosulfonic acid (TAPPI, T 629 m-53); lignosulfonic acid+cation equivalent of SO_3 in lignosulfonic acid=lignosulfonate salt.

[4] Calculated as glucose.

[5] Total carbohydrates—reducing sugars.

[6] May include such wood sugars as mannose, glucose, xylose, galactose, arabinose and fructose.

[7] Estimated by difference.

[8] Derived from Kraft process.

[9] Maximum possible. The empirical calculation gave unreasonably large values because of high methoxyl contents.

[10] Established as sucrose by infrared spectral analysis.

[11] Probably alkyl aryl sulfonate salt.

[12] Calculated from total nitrogen content.

Ultraviolet Spectral Analysis

Each material was analyzed by ultraviolet spectroscopy to determine if it could be identified or characterized by its ultraviolet absorption spectrum. The apparatus used for ultraviolet work included a double beam quartz spectrophotometer, an ultraviolet power supply unit, and a hydrogen discharge lamp as a light source. Measurements were made in 1 cm. matched silica rectangular cells.

Procedure for lignosulfonates

Special buffer.—495 ml. of 0.2 N KH_2PO_4 and 113 ml. of 0.1 N NaOH were mixed and diluted to 2 liters.

Sample preparation.—0.5 g. of solid sample or exactly 1 ml. of liquid sample was dissolved and diluted with water to 100 ml. Insoluble material was removed by centrifuging. A 10 ml. clear aliquot was diluted to 100 ml., and finally a 1 ml. aliquot of the latter was diluted to exactly 10 ml. with the buffer solution. Final concentration was 0.005 percent by weight or 0.01 percent by volume in the case of the liquid samples.

Measurements.—Absorbance for each material was measured at intervals between 220 and 350 millimicrons in 1 cm. cells. Readings

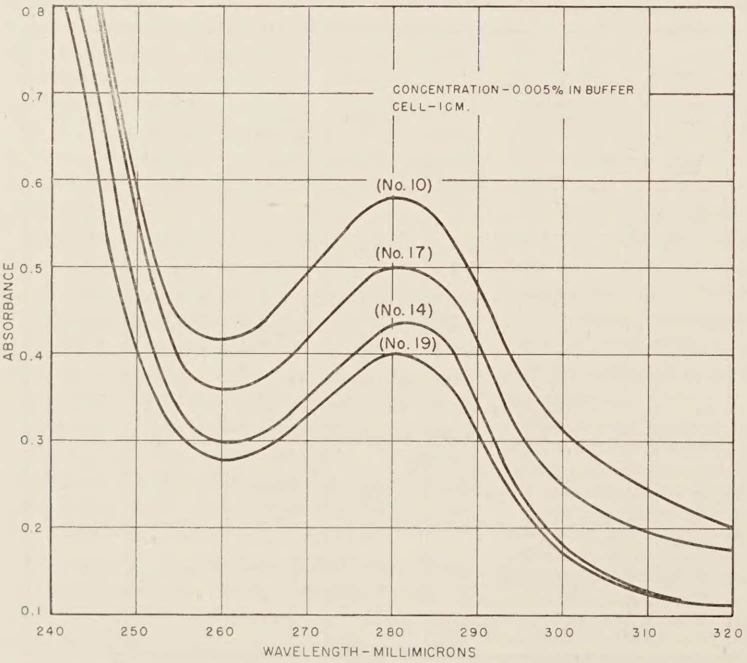

Figure 2.—Typical ultraviolet spectra of lignosulfonates.

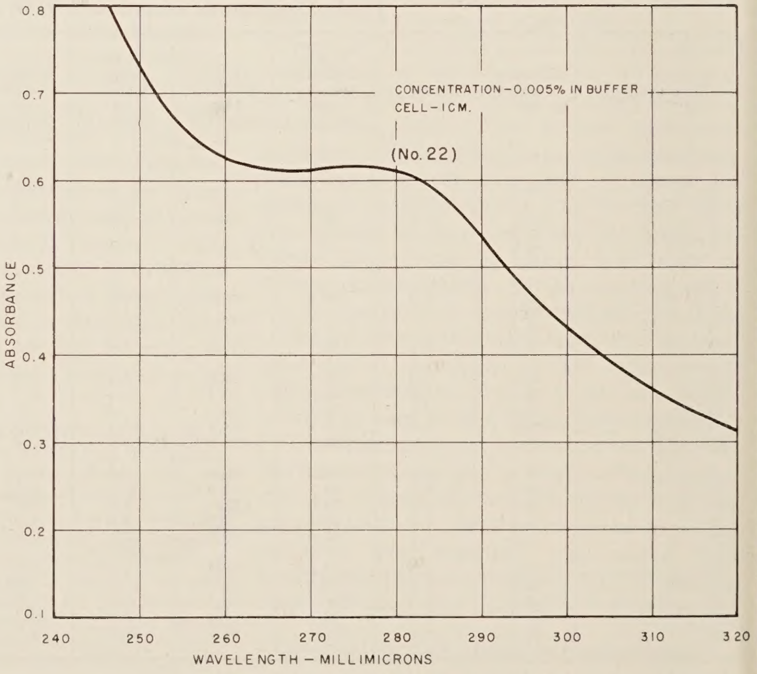

Figure 3.—Ultraviolet spectrum of lignosulfonate from Kraft process.

were made at wavelength intervals of 5 to 10 millimicrons, except where peaks appeared near 260 and 280 millimicrons. In these areas, readings were obtained at 0.5 to 1.0 millimicron intervals. The sensitivity of the instrument was adjusted so as to maintain the smallest slit openings. The lamp housing was cooled with circulating tap water.

Plotting.—The absorbance readings were plotted against wavelength and the resultant spectral curve was then drawn manually. Absorbance is defined as $\log_{10} I_o/I$, where I_o equals incident radiant power, and I equals transmitted radiant power.

Results of tests on lignosulfonates

Figure 2 shows examples of typical ultraviolet spectra obtained on several lignosulfonate retarders. The shape of each curve was typical of all the other lignosulfonate retarders except one, retarder No. 22, which had been derived from the Kraft process. The spectrum of sample No. 22, shown separately in figure 3, indicated a shoulder rather than a peak occurred at 280 millimicrons. It thus appeared that lignosulfonates as a class could be identified from their characteristic ultraviolet spectra. In addition, the height of the peak (absorbance) at 280 millimicrons could be utilized for quantitative information. Figure 4 shows that lignosulfonate concentration and absorbance values have a linear relationship in accord with Beer's law. These tests confirm previous reports that lignosulfonates may be analyzed quantitatively as well as qualitatively by ultraviolet spectrophotometry (*9*).

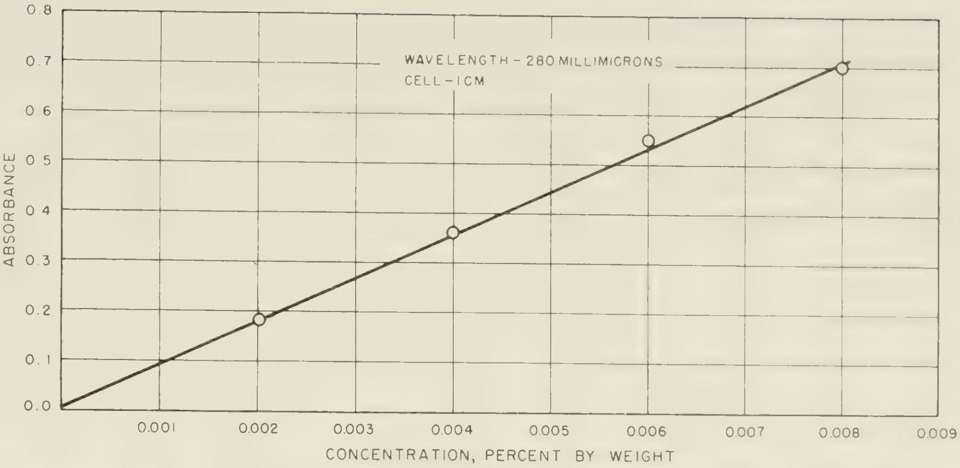

Figure 4.—Relation between concentration and absorbance for lignosulfonate retarder.

Table 6 gives the ultraviolet spectral data for all the lignosulfonate retarders tested. It can be seen from this table that the peaks for each material occurred within a narrow wavelength range.

Results on the other chemical types

None of the other types of retarders studied had a significant ultraviolet spectrum that was characteristic of the active constituent. Retarder No. 1 did have a characteristic spectrum which was produced by a minor constituent, phenol. Generally, however, ultraviolet spectral analysis was not found suitable for identifying organic hydroxy-carboxylic acids or carbohydrates.

Investigation of Visible Spectra

The double beam quartz spectrophotometer with a tungsten lamp as a light source was used to investigate the visible spectra of the materials other than lignosulfonates. The spectral patterns obtained are shown in figure 5. Each spectrum is not sufficiently unique to differentiate between different retarder types or specific retarders. It was found that phenol, sucrose, and even triethanolamine gave spectra similar to those shown in figure 5 and, consequently, this approach was also not suitable for identifying retarders.

Infrared Spectra

Infrared spectral curves were obtained for each material by means of a double-beam spectrophotometer. The equipment used included a Perkin-Elmer double-beam Infrared Spectrophotometer, Model 137 (Infracord), with automatic recording and a sodium chloride prism for operation between 2.5 and 15 microns. Scanning time was approximately 12 minutes. An evacuable die was used to prepare samples by the potassium bromide disk technique.

Procedure

The pressed disk technique was considered most suitable for the retarders studied because of the relative insolubility of these materials in appropriate organic solvents used in solution techniques. The mull method was discarded because of the effects of the mulling agent and the limited quantitative application of this method.

In the pressed disk method, solid samples were ground to a fine powder with mortar and pestle and then vacuum dried at 50° C. for at least 24 hours. Liquid samples were evaporated to dryness at a low temperature, ground, and dried under the same conditions. Approximately 1 mg. of sample and 0.35 g. of potassium bromide (anhydrous spectroscopic grade, 200/325 mesh) were weighed into a special stainless steel capsule. Two stainless steel balls were added and the contents mixed for 30 seconds by an electric amalgamator.

The powder was transferred to the evacuable die (shown disassembled in figure 6), and the assembly was evacuated to an absolute pressure of less than 1 cm. of mercury. Vacuum was maintained for 5 minutes prior to pressing as well as during pressing. A 1,000-pound load was applied for 1–2 minutes followed by a 20,000 pound load for 3–5 minutes. The potassium bromide disk was then removed and analyzed in the infrared spectrophotometer. The disk measured 13 millimeters in diameter and was approximately one millimeter thick and is shown in figure 7.

A few of the dried retarder samples were tacky or viscous. These were slurried with alcohol, mixed with potassium bromide, vacuum dried, and then reground and pressed into disks.

Table 6.—Ultraviolet spectral data for lignosulfonate retarders

Retarder No.	Final concentration[1] (percent)	Spectral peaks[2]				Relative concentration of lignosulfonate, percent by weight[7]	
		Maximum		Minimum			
		Wavelength (millimicrons)	Absorbance	Wavelength (millimicrons)	Absorbance	Based on original material	Based on dry solids
2	0.05	281.0	0.151	260.5	0.121	2.0	2.0
3	.005	278.0	.457	262.5	.396	60.9	65.3
7	.005	280.5	.589	259.5	.431	78.5	82.2
10	.005	280.0	.582	260.0	.419	77.6	81.8
11	.005	283.0	.362	260.0	.225	48.3	51.5
12	.005	280.0	.474	261.0	.395	63.2	66.1
13	.005	279.0	.328	262.0	.292	43.7	47.9
14	.005	282.0	.438	261.0	.298	58.4	62.4
15	.005	278.0	.442	262.0	.390	58.9	63.6
16	.005	281.5	.408	260.5	.281	54.4	57.4
17	.005	280.5	.502	260.0	.359	66.9	72.4
18	.005	281.0	.393	260.5	.272	52.4	56.5
19	.005	280.0	.400	260.0	.278	53.3	56.3
20	[5].01	279.0	.333	262.5	.284	19.1	61.6
21	[5].01	280.0	.290	260.5	.248	16.8	56.6
22[3]	.005	[6]276.0	.618	[6]267.5	.611	82.4	90.1
23	.005	280.0	.460	260.5	.384	61.3	66.1
24	.005	284.0	.381	262.5	.297	50.8	52.9
25	.005	281.5	.441	261.0	.308	58.8	62.9
Median[4]	--------	280.0	----------	260.5	----------	--------	--------

[1] In 0.2N KH_2PO_4–0.1N NaOH buffer solution.
[2] 1 cm. cell.
[3] Derived from the Kraft process.
[4] Retarder No. 22 not included.
[5] Percentage by volume (original material was liquid).
[6] No sharp maximum and minimum, but rather a shoulder.
[7] Calculated from absorbance at maximum peak. Relative to retarder No. 2 which was assumed to be 2 percent.

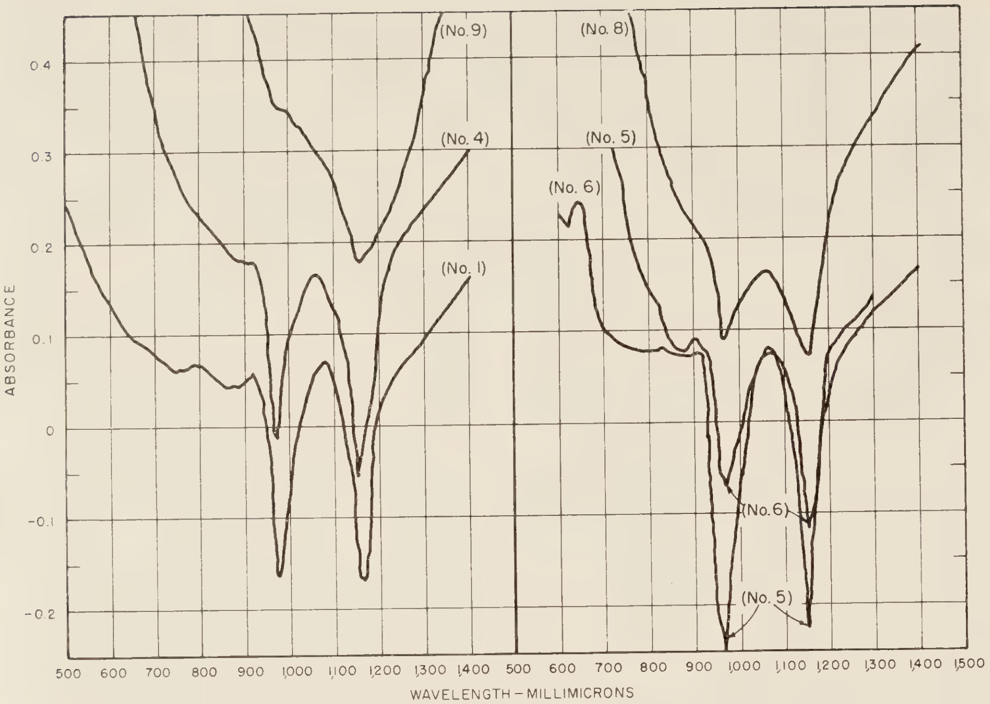

Figure 5.—Visible spectra of retarders containing organic acids or carbohydrates.

Results of infrared analyses

Figures 8 through 12 illustrate typical infrared spectra of the different retarders. Each retarder gave a characteristic spectrum which could be used both to identify the material and establish the concentration of major active constituents. In general, lignosulfonate retarders had the same characteristic spectra regardless of the type of salt (i.e., sodium, calcium, or ammonium). Nevertheless, certain lignosulfonates containing carbonates or other major modifiers, as well as a lignosulfonate derived from the Kraft process, could be easily distinguished by their unique spectra.

Figure 8 shows the type of spectra obtained for the lignosulfonate type retarders. The top spectrum (A), retarder No. 12, illustrates the typical spectrum of lignosulfonates derived from the sulfite liquor or acid process. The characteristic peaks at different wavelengths in the lignosulfonate spectrum are produced by the following chemical groupings present:

1. Intense peaks at 2.9 and 9.6 microns: hydroxyl (OH) groups.
2. Moderate peak at 3.4 microns: usual carbon-hydrogen stretching bonds.
3. Strong peaks at 6.25 and 6.62 microns: carbon-carbon bonds (phenyl ring).
4. Weak peaks at 6.9 and 7.3 microns: probably sulfur-oxygen bond (sulfone group).
5. Broad band at approximately 8.3 microns: sulfonate group.

Spectrum B, figure 8, is the curve for lignosulfonate retarder No. 13. The presence of substantial amounts of sodium carbonate produced strong bands which masked part of the characteristic lignosulfonate spectra. The broad peaks at 7.0 and 11.3 are characteristic of the sodium carbonate present (see figure 9A which illustrates the infrared pattern of sodium carbonate). If desired, the sodium carbonate interference may be removed by neutralization with hydrochloric acid, followed by an alcohol extraction of the sodium chloride thus formed. The lignosulfonate is insoluble in alcohol and should then give a good characteristic spectrum.

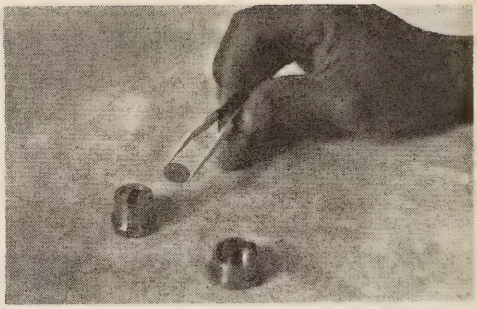

Figure 7.—Potassium bromide disk and disk holder.

Curve C in figure 8 represents a lignosulfonate (No. 22) obtained from the Kraft process for making paper. Although the curve shows the major peaks of a typical lignosulfonate, several additional characteristics help identify this material. For instance, at 8.3 microns (sulfonate group) absorption was at a greater intensity, and at 8.8 and 10.2 microns peaks were produced, probably by inorganic sulfate. Another characterization of this material was the weak absorption peak at 12.7 microns.

The last two spectra, D and E, in figure 8 are of the same sample (No. 2), which contained a lignosulfonate. Curve D was obtained on the original sample, and it is

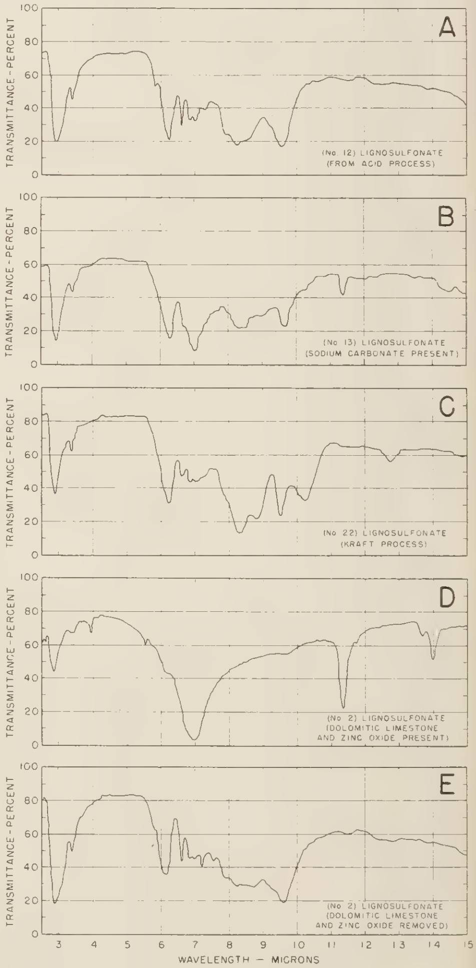

Figure 8.—Typical infrared spectra of lignosulfonate retarders.

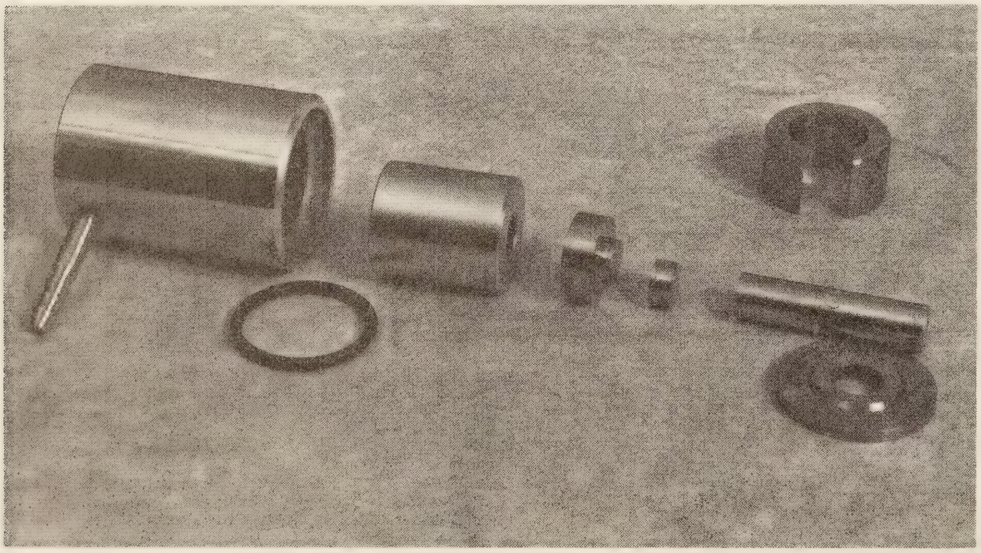

Figure 6.—Evacuable die disassembled.

apparent that it does not clearly show the characteristic lignosulfonate pattern. This was caused by the presence of a large quantity of dolomitic limestone which produced an intense spectrum of its own. When this constituent was removed by centrifuging an aqueous suspension, the characteristic spectrum of lignosulfonate was evident as shown in curve E. Spectrum D is useful in that it supplied ample evidence of the presence of dolomitic limestone in the original material. The peak at 14 microns was unique for calcium carbonate (limestone), while the smaller peak at 13.7 microns was unique for dolomite. From the relative intensities of these two peaks it was estimated that the ratio of dolomite to limestone was approximately 1:4.

Figure 9 shows the spectra obtained on several carbonate materials, namely, sodium carbonate, calcium carbonate, and dolomite. Spectra B and C illustrate the characteristic peaks for limestone and dolomite discussed above.

Figure 10 illustrates the unique infrared patterns which may be used to identify different hydroxy-carboxylic acid salts. It is quite apparent that these curves are distinctly different from the lignosulfonate pattern as well as from each other. Spectrum A (retarder No. 8) shows the masking effect of a large amount of siliceous matter and iron oxide present in the material. To eliminate this interference, an aqueous suspension of the retarder was centrifuged to remove insoluble siliceous material and iron oxide. The remaining material then gave a distinctive infrared pattern of organic material as seen in spectrum B. The following chemical groups accounted for the more significant peaks in spectrum B: (1) Hydroxyl—intense peak at 3.1 microns; (2) carbon-hydrogen stretching—minor peak at 3.4 microns; (3) carboxyl and carboxyl salt—intense peaks at 6.3, 9.1, and 9.6 microns; and (4) overtones of the carbon-hydrogen linkages accounted for the other peaks from 7.3 to 8.3 microns.

The spectrum of a triethanolamine salt of a hydroxy-carboxylic acid is shown in spectrum C, figure 10. Although the major peaks of hydroxyl, carbon-hydrogen, and carboxylic groups were evident, this spectrum had sufficiently unique features to clearly identify the retarder. For instance, there was a prominent peak at 10.9 microns, probably caused by a carbon-nitrogen bond, and the usual hydroxyl peak at 3.0 microns was accentuated by the presence of nitrogen-hydrogen groups in this material.

Figure 11 shows the spectra of still another organic acid retarder (No. 6). Curve A shows the spectrum of the original material, whereas Curve B was obtained after zinc and borates were removed. Zinc was removed by two batchwise treatments with a cation exchange resin, 200–400 mesh hydrogen-form (Amberlite IR–120 or Dowex–50) followed by vacuum distillation with methyl alcohol to remove the boron as volatile methyl borate (*10*). Spectrum B shows many of the usual peaks of a hydroxy-carboxylic acid, and is sufficiently distinctive to be used to identify this material. The prominent peak at 5.6 microns was undoubtedly caused by a lactone formation. Spectrum C in the same figure is that of a technical grade of gluconic acid which showed a striking resemblance to sample No. 6 (spectrum B).

The infrared spectrum of the carbohydrate retarder is illustrated in figure 12. Spectrum A (retarder No. 1) presents a pattern that was quite unique and therefore useful for identification. A comparison of this spectrum with the spectrum of sucrose or cane sugar (curve B) clearly demonstrates that retarder No. 1 is essentially sucrose.

Although no effort was made in this report to use the infrared spectra for quantitative analysis of the materials, such techniques could be easily applied. For solid samples, such as potassium bromide pellets, the baseline technique is most appropriate and has been well described. Generally, this technique involves the measurement of the depth of a single significant peak, compared to a reference base line.

Uniformity of trade products

The ability of infrared analysis to "fingerprint" or measure the uniformity of different batches of specific proprietary products is illustrated by figures 13 and 14. Figure 13 shows the spectra of four different lots of a solid lignosulfonate retarder sold under one trade name. Each material had been obtained from a supplier by different State highway departments at different times ranging from 1954 (fig. 13A) to 1958 (fig. 13D). The general shape of the spectra are the same, with signifi-

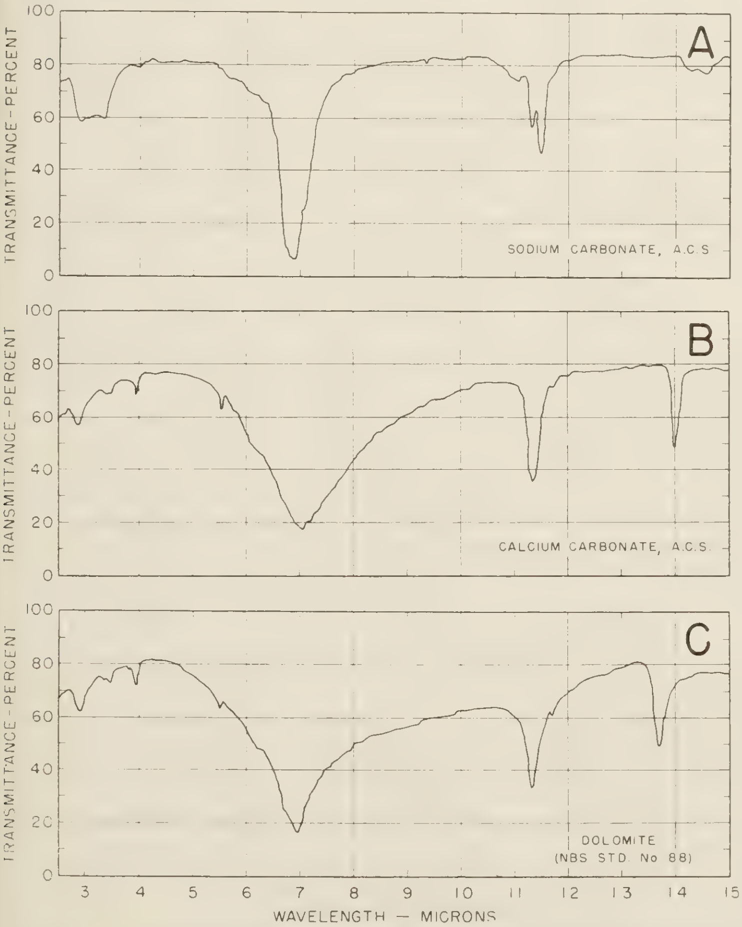

Figure 9.—Infrared spectra of related inorganic carbonates.

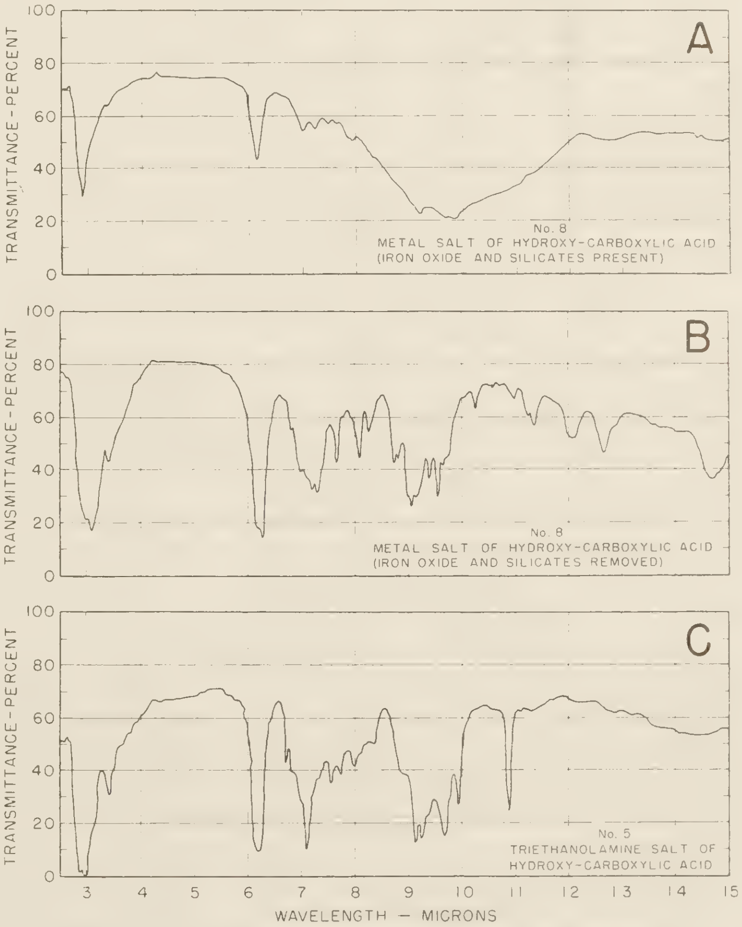

Figure 10.—Infrared spectra of organic acid retarders.

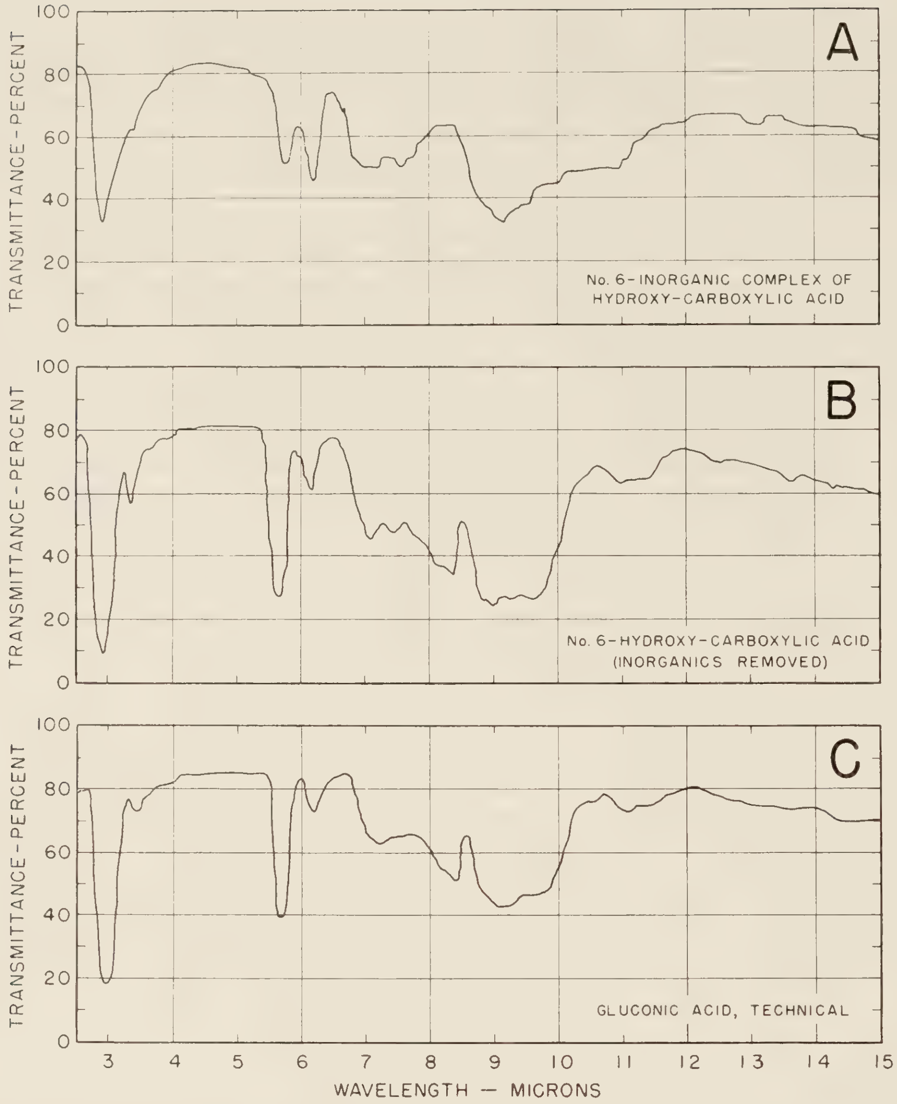

Figure 11 (to the left).—Infrared spectra of complexed organic acid retarder and gluconic acid.

cant peaks occurring at the same wavelengths in each lot This definitely established that in each case the materials were chemically the same. By analyzing the peak intensities at selected wavelengths and knowing the concentration of sample used in the infrared analysis, any material differences in composition of the retarder from batch-to-batch could be demonstrated. Here, the compositions were shown to be fairly uniform, thus establishing that no material alteration or differences existed between the lots submitted.

Figure 14 shows the spectra for an organic acid retarder, specifically, a hydroxy-carboxylic acid salt in liquid form. Here again, each sample was obtained under the same trade name by different State highway departments at different times ranging from 1956 (fig. 14A) to 1958 (fig. 14D). The "fingerprinting" ability of infrared analysis once again determined the nature and concentration of the ingredients. The uniformity of the spectra shows that each lot was substantially the same.

Comparison of Methods of Analyses

Since the major objective of this study was to develop procedures by which the composition of commercial retarders could be readily identified and determined so as to provide a basis for obtaining the necessary assurance that the composition would be uniform from batch-to-batch, it is noteworthy to compare the various methods of analyses.

Infrared spectral analyses offers the most promising and rapid means of clearly identifying and classifying retarder materials. This technique, by obtaining recorded spectral curves, "fingerprints" the unique and distinctive characteristics for each retarder. Thus, carbohydrates and organic hydroxy-carboxylic acids were easily identified due to their distinctive spectral patterns. Lignosulfonates likewise had unique characteristics which made identification easy, regardless of the type or salt present or the source of supply. Further, spectral difference caused by the manufacturing process or the presence of other ingredients aided in the identification and determination.

Infrared analyses can also be used to assure the purchaser that the nature and concentration of each lot of retarder for specific field projects has not been materially altered from that of the original material. The time required for the analysis is only 20 to 30 minutes as compared to a week or more by conventional methods of chemical analysis.

Ultraviolet techniques were also found to be of value in identifying lignosulfonates and in establishing the concentration of the major active ingredient. However, specific commercial lignosulfonates were not as easily differentiated by ultraviolet spectra as compared to their infrared spectra. Ultraviolet as well as visible spectral analyses were not found suitable for identifying other types of retarders.

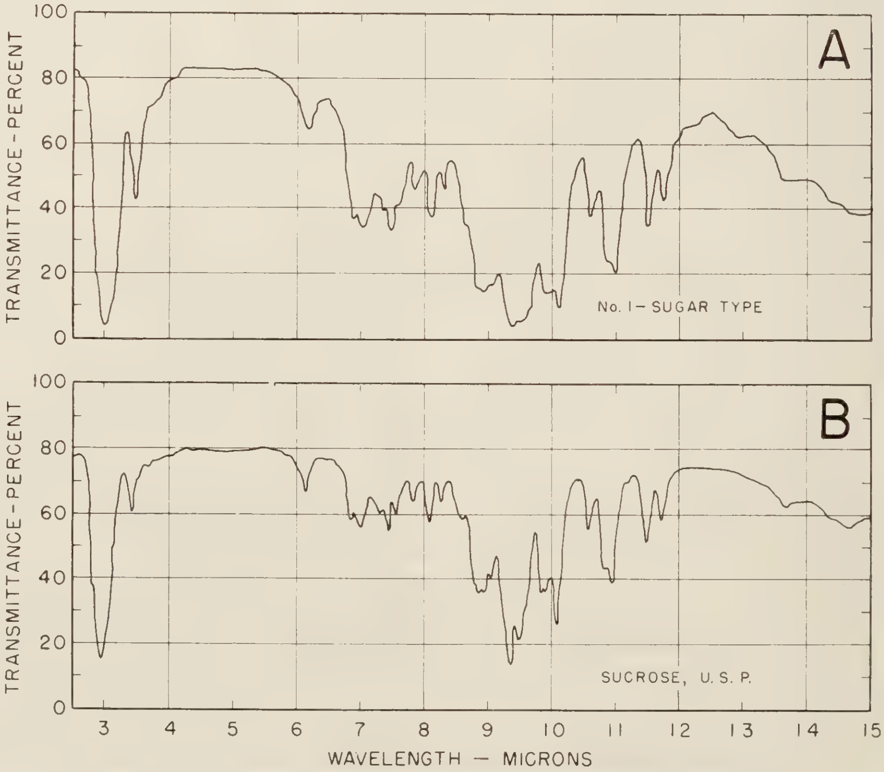

Figure 12.—Infrared spectra of carbohydrate retarder and sucrose.

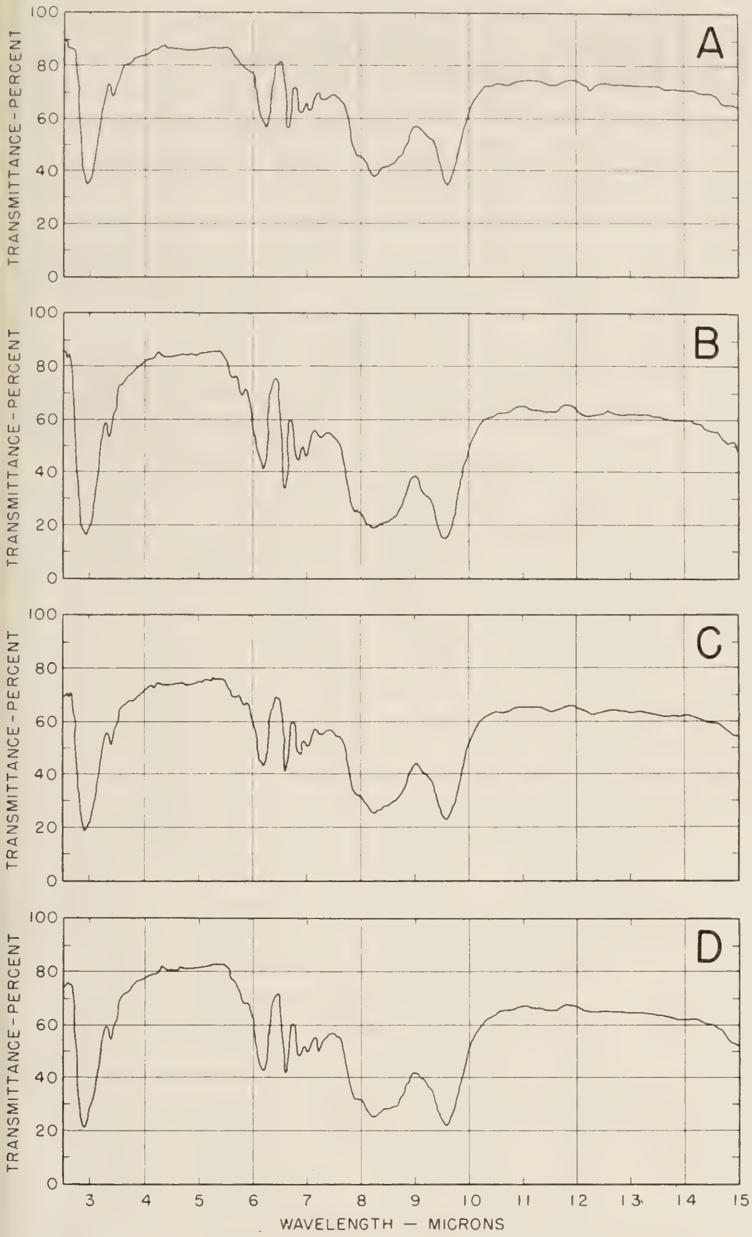

Figure 13.—Infrared spectra of four different lots of a lignosulfonate retarder obtained from one manufacturer.

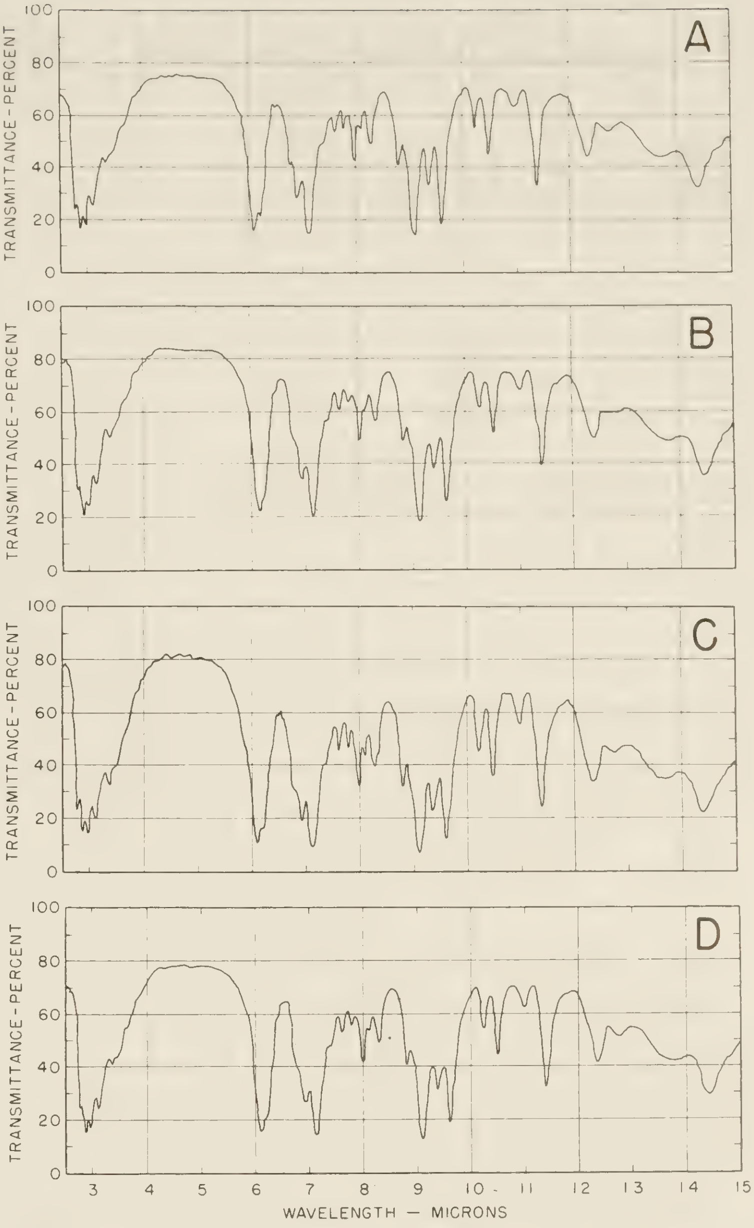

Figure 14.—Infrared spectra of four different lots of an organic acid retarder obtained from one manufacturer.

The determination of the quantitative amounts of inorganic constituents can be most conveniently and precisely determined by conventional chemical methods. However, while useful, the conventional procedures were tedious and time-consuming, and often yielded empirical or doubtful results for certain organic constituents. This was found to be particularly true among the lignosulfonate and organic acid retarders.

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Water-Reducing Retarders for Concrete—Physical Tests

BY THE DIVISION OF PHYSICAL RESEARCH
BUREAU OF PUBLIC ROADS

Reported[1] by
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THE USE OF CHEMICALS for delaying the initial setting time of portland cement concrete is not new. The effects of sugar and other retarders on concrete have been known for many years. In 1945, it was reported that a retardant admixture had been used during 1942 to 1945 in lightweight concrete for the construction of concrete ships (*1*)[2]. The admixture was used in non-air entrained concrete to reduce the amount of mixing water, or to increase slump and to prevent the early stiffening and formation of "cold joints."

Since that time there have been many articles written discussing the use of retardants in concrete for prestressed beams or piles and bridge structures and relating valuable test data (*2, 3*).

Several Federal agencies have been using temporary or interim specifications for retarders. The Bureau of Reclamation suggested a specification in 1954 and the Bureau of Public Roads proposed a specification for certain local usage in 1956 which was revised in 1958. These specifications were based mainly on field experiences with retarders from two manufacturers, and on a limited amount of laboratory test data. The need for a specification for commercially available retarders has become greater since the possible benefits of retarders have been recognized more fully.

Concrete Materials Used

The classification of the 25 retarders tested and their general properties are shown in table 1. The information supplied by the marketer and tests by the Bureau were the bases for the classification.

A blend of equal parts by weight of four brands of type I cement was used for all concretes in this investigation. The chemical composition and physical properties of each brand and of the blend are shown in table 2. About 32 bags (one lot) of each of the four cements were stored in sealed 55-gallon steel drums until used, and three lots of each of the four cements were used altogether during the investigation.

The air entraining admixture used was an aqueous solution of neutralized Vinsol resin. The solution contained 15 percent of solids when calculated as a residue dried at 105° C., and the ratio of sodium hydroxide to Vinsol resin was 1 to 6.4 parts by weight.

A natural siliceous sand having a fineness modulus of 2.90, a specific gravity (bulk dry) of 2.65, and an absorption of 0.4 percent, and a crushed limestone of 1-inch maximum size, having a specific gravity (bulk dry) of 2.75 and an absorption of 0.4 percent, were used as aggregates. When the aggregates for a batch of concrete were weighed, the sand contained free water but the stone was weighed in a saturated surface-dry condition.

Three mixes of air-entrained concrete with air contents of 5 to 6 percent and a slump of 2 to 3 inches were used in the study. Mix No. 1, the reference mix without retarder, and mix No. 2, a test mix with retarder, had cement contents of 6 bags per cubic yard of concrete. Mix No. 3, also a test mix with retarder, had cement contents which varied from 5.25 to 5.75 bags per cubic yard and the water-cement ratio was approximately the same as that of the reference mix (No. 1). The water content of mix No. 2 was reduced below that of the reference mix but sufficient aggregates were added to compensate for the reduced volume. A summary of the mix proportions is given in table 3.

A sufficient amount of retarder was used in the tests of mix No. 2 at 73° F. to cause a delay in setting time of 2½ to 3 hours beyond the setting time of the reference mix. The correct amount of each retarder for the desired retardation was predetermined by trial mixes. The same amount of retarder, in ounces per

Table 1.—Properties of retarders

Type of retarder	Retarder No.	Physical state	Amount of retarder: Recommended by manufacturer	Amount of retarder: Used [1]	Retarder constituents [2]: Dry solids [3]	Retarder constituents [2]: Volatile organic material [4]
Lignosulfonates:			*Oz./bag*	*Oz./bag*	*Oz./bag*	*Oz./bag*
Ammonium salts	7	Powder	--------	3.5	3.3	3.3
	10	do	3.8	3.2	3.0	3.0
	[5 6] 17	do	--------	3.2	3.0	2.9
Sodium salts	15	Powder	3.8- 7.5	4.0	3.7	2.8
	19	do	4.0	4.0	3.8	2.8
	[7] 22	do	.8	4.0	3.7	2.0
	23	do	3.8	6.4	5.9	3.9
Calcium salts	[8] 2	Powder	8.0	14.4	14.3	.40
	3	do	3.8- 7.5	4.0	3.7	3.1
	[9] 11	do	4.0	4.8	4.5	3.2
	12	do	--------	4.0	3.8	3.0
	13	do	4.5- 7.5	4.8	4.4	2.3
	[6] 14	do	3 - 4	5.0	4.7	4.0
	16	do	4.0	4.8	4.5	3.8
	18	do	4.0- 5.0	4.0	3.7	3.4
	20	Liquid	9.0	9.0	3.3	2.6
	21	do	9.0	9.0	3.2	2.5
	[9] 24	Powder	12.0	9.6	9.2	5.1
	[5 10] 25	do	3 - 4	4.0	3.7	3.1
Organic acids:						
Metal salts	4	Liquid	2.0- 4.0	3.0	1.2	.88
	8	Powder	8.0-16.0	12.0	11.9	1.2
	[11] 9	Liquid	2.0- 4.0	2.8	1.1	.77
Triethanolamine salt	5	Liquid	2.7- 7.1	4.0	2.1	2.1
Zinc borate complex	6	do	2.0	4.0	1.3	.91
Carbohydrates: Sucrose	[5] 1	Liquid	1.0- 4.0	1.1	.4	.43

[1] Amount of retarder necessary to retard set of concrete from 2½ to 3 hours as determined by Proctor penetration test at 500 p.s.i.
[2] Additional chemical constituents reported in footnotes.
[3] Determined by drying at 110° C.
[4] Determined by ignition.
[5] Over 10 percent carbohydrate.
[6] Over 5 percent reducing sugar.
[7] Derived from Kraft process.
[8] Contained less than 5 percent calcium lignosulfonate.
[9] Contained calcium chloride.
[10] Contained foaming agent.
[11] Contained less than 10 percent of active organic constituent. Remainder is iron oxide and siliceous material.

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[1] Presented at the 40th Annual Meeting of the Highway Research Board, Washington, D.C., January 1961.

[2] Italic numbers in parentheses refer to a list of references on page 154.

Table 2.—Chemical composition and physical properties of portland cement

Determination [1]	Cement A	Cement B	Cement C	Cement D	Blend [2]
Chemical composition (percent):					
Silicon dioxide	21.4	21.4	21.9	21.4	21.6
Aluminum oxide	5.9	5.1	5.6	5.4	5.4
Ferric oxide	2.8	2.2	2.3	2.4	2.4
Calcium oxide	63.4	62.5	66.1	65.2	64.3
Magnesium oxide	2.1	3.8	1.2	1.6	2.2
Sulfur trioxide	1.8	2.4	1.7	1.9	2.0
Loss on ignition	1.7	1.5	1.2	1.1	1.4
Sodium oxide	.20	.30	.02	.14	.18
Potassium oxide	.82	.95	.14	.79	.69
Equivalent alkalies as Na_2O	.74	.93	.11	.66	.63
Chloroform-soluble organic substances	.016	.008	.004	.007	.008
Free lime	.97	.93	.97	.66	.94
Computed compound composition (percent):					
Tricalcium silicate	47	48	57	58	52
Dicalcium silicate	26	26	20	18	23
Tricalcium aluminate	11	10	11	10	10
Tetracalcium aluminoferrite	8.5	6.7	7.0	7.3	7.4
Calcium sulfate	3.05	4.08	2.89	3.23	3.31
Merriman sugar test:					
Neutral point, ml	7.6	2.4	2.3	2.5	3.3
Clear point, ml	8.8	2.8	2.6	2.8	4.2
Physical properties:					
Apparent specific gravity	3.12	3.13	3.14	3.14	3.12
Specific surface (permeability), cm.²/g	3,375	3.590	3.110	3.145	3.310
Autoclave expansion, percent	.07	.19	.04	.06	.07
Normal consistency, percent	25.3	24.3	24.4	24.6	24.0
Time of setting (Gillmore test):					
Initial, hours	2.9	2.8	3.4	4.0	2.3
Final, hours	6.2	5.1	6.8	6.0	7.5
Compressive strength:					
At 3 days, p.s.i	2,500	2,500	2,030	2,610	2,490
At 7 days, p.s.i	4,165	3,450	3,225	4,175	3,840
At 28 days, p.s.i	5,690	4,565	5,585	5,510	5,285
Tensile strength:					
At 3 days, p.s.i	340	320	300	320	315
At 7 days, p.s.i	400	395	365	435	400
At 28 days, p.s.i	470	465	475	465	480
Mortar air content, percent	8.0	8.8	7.5	7.8	8.6

[1] All determinations except the Merriman sugar test were made in accordance with current AASHO methods for portland cement.

[2] Tests made on blend of equal parts by weight of all four cements.

bag of cement, was used in mix No. 3. Additional tests of some retarders were made using four times the amount of the retarder used in mixes Nos. 2 and 3.

Mixing, Fabrication, and Curing of Specimens

Mixing was done in an open-pan type Lancaster mixer with a rated capacity of 1¾ cubic feet. Most batches were from 1½ to 2 cubic feet in volume. The mixing cycle was as follows: The blend of four cements and the moist fine aggregate were mixed for 30 seconds; water was added and the mortar was mixed for 1 minute. After the addition of the coarse aggregate the concrete was mixed for 2 minutes. Following a rest period of 2 minutes, the concrete was mixed for 1 more minute. This 2-minute rest period and the additional minute of mixing is standard laboratory procedure for the Bureau of Public Roads.

Retarder in powder form was added with the cement and sand, but a liquid retardant admixture was added with part of the mixing water. Vinsol resin solution was added with part of the mixing water, but was not mixed with the liquid retarder until each was placed in the mixer.

Consideration was given to adding the soluble powdered admixtures in an aqueous solution. Although the soluble powders could have been prepared in a stock solution or suspension, it was believed that during the period of months required for the program, evaporation or chemical changes of the solution of the retarder due to exposure to light might result. An attempt was made to dissolve in water the weighed amount of lignosulfonate powder required for a single batch of concrete but difficulty was experienced with some powders in obtaining a uniform solution or suspension. Therefore, the procedure of adding the powdered admixture with the cement and wet sand was used. It was believed that a uniform distribution of the powdered admixture in the concrete was obtained.

A control or reference mix (No. 1) was made on each mixing day together with the retarder mixes (Nos. 2 and 3). Due to time and mold limitations only one control mix and two retarder test mixes were made on each mixing day for each of three to five different retarders. Two rounds of specimens for retardation tests and five rounds for strength tests were made but each round did not necessarily include the same retarders as in the preceding round.

Concrete used for slump and unit weight tests was returned to the mixer and remixed for 15 seconds before molding specimens for strength tests. Concrete used in the air meter was discarded. Specimens made at standard conditions were mixed and molded in a temperature of 73° F. and 50 percent relative humidity.

Specimens for strength or durability tests were 6- by 12-inch cylinders and 6- by 6- by 21-inch or 3- by 4- by 16-inch beams. These were molded (except for vibrated specimens) in accordance with standard AASHO methods. Specimens for strength tests were removed from the steel molds at 20 to 24 hours. Small beams for volume change and freezing and thawing were removed from the steel molds at 44 to 48 hours.

For a study of delayed vibration, 6- by 12-inch cylinders and 6- by 6- by 21-inch beams were molded by the standard procedure and later vibrated for 30 seconds using an internal spud vibrator of 1⅛-inch diameter with a frequency of 7,000 impulses per minute.

The original program required that the specimens be vibrated when the screened mortar showed a Proctor penetration[3] load of 500 p.s.i., which was approximately 5 hours after mixing for unretarded concrete and 7½ to 8 hours for the retarded concretes. However, the prescribed time intervals proved too long as the mixes became too stiff for vibration. Therefore, the time intervals were reduced to 3 hours after mixing for the nonretarded concrete and 5½ hours for the retarded concrete. A small amount of concrete was removed from each specimen just prior to vibration and it was replaced as the vibration was completed. No additional concrete was added to compensate for the decrease in volume.

All specimens for standard strength tests were cured under wet burlap while in the molds in the mixing room. After removal from the molds they were cured in moist air at 73° F. and 100 percent relative humidity until they were tested. Small beams for volume change and freezing and thawing were cured in the molds for 44 to 48 hours under wet burlap in the moist room. One-third of the beams for volume change was cured continuously in the moist room, one-third were removed from the moist room at 2 days and stored in laboratory air at 73° F. and 50 percent relative humidity, and one-third were cured 14 days in the moist room and

Table 3.—Summary of concrete mix proportions

Properties of concrete	Mix No. 1	Mix No. 2 [1]	Mix No. 3 [2]		
			Group A	Group B	Group C
Mix:					
Cement, pounds	94	94	94	94	94
Sand, pounds	190	193	205	215	230
Limestone, pounds	310	314	330	345	360
Cement, bags per cubic yard	6.0	6.0	5.75	5.50	5.25
Water, gallons per bag	5.8	5.1–5.7	5.8	5.8	5.8
Water-cement ratio, by volume	.77	.68–.76	.77	.77	.77
Slump, inches	2½	2½	2½	2½	2½
Air, percent	5.5	5.5	5.5	5.5	5.5
Retarder, amount used	None	(³)	(³)	(³)	(³)

[1] Mix No. 2 had same cement content as Mix No. 1.

[2] Mix No. 3 had same water-cement ratio (±0.2 gal/bag) as Mix No. 1. Group A—cement content reduced 0.25 bag per cubic yard for retarders that reduced water for Mix No. 2 by up to 5 percent. Group B—cement content reduced 0.50 bag per cubic yard for retarders that reduced water for Mix No. 2 by 5 to 10 percent. Group C—cement content reduced 0.75 bag per cubic yard for retarders that reduced water for Mix No. 2 by 10 percent or more.

[3] To give 2½ to 3 hours retardation.

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[3] A method of testing for rate of hardening of mortars sieved from concrete mixtures by Proctor penetration resistance needles in accordance with ASTM Method C 403-57 T. This method is referred to as the Proctor penetration method.

then stored in laboratory air. Beams for freezing and thawing, after removal from the molds at 44 to 48 hours, were cured in the moist room for 12 more days, then cured in laboratory air at 73° F. and 50 percent relative humidity for 7 days and then were completely immersed in water for 7 days prior to freezing.

When strength specimens were made under nonstandard atmospheric conditions, the laboratory air temperature was 90° F. and the relative humidity was 20 to 25 percent. All materials were at 90° F. when used. After 20 to 24 hours curing under wet burlap at this temperature, the specimens were removed from the molds and stored in the moist room at 73° F. and 100 percent relative humidity until tested.

Testing Procedures

Tests on the plastic concrete for slump, unit weight, and air content were made in accordance with AASHO standard methods. The determination of the air content was made with a water-type pressure meter that is similar to the meter described in AASHO Method T 152.

Determination of the retardation of the set of concrete was made by the Proctor penetration method and by the bond pin pullout method.[4] The Proctor penetration apparatus with a hydraulic indicating dial and the pin pullout device are shown in figures 1 and 2. Both apparatus were constructed by the Bureau of Public Roads.

The mortar for the Proctor penetration method was obtained by sieving the plastic concrete on a No. 4 sieve. The sieve was vibrated and the concrete was moved over the sieve by hand or by use of a small trowel. Two 6- by 6-inch watertight steel cylinder molds were filled with mortar, and were immediately covered with glass plates. Water was pipetted from the mortar as it collected on the surface.

Concrete for the pin pullout test was vibrated around the pins in a 6- by 6- by 24-inch mold using a laboratory internal vibrator, and was screeded on the surface by a steel straight edge. The specimens were covered with wet burlap which was removed only while a pin was pulled from the concrete. No two consecutively pulled pins were adjacent to each other.

Typical curves for retardation of mixes Nos. 1 and 2 by the Proctor penetration and pin pullout methods are shown in figure 3.

Two series of tests were made to determine the temperature rise of concrete prepared with retarders. In the first series of tests, 6- by 6-inch cardboard cylinder molds were filled with screened mortar from concrete that was mixed at 90° F. The specimens were then sealed by a glass plate and heavy grease and stored in a curing cabinet at 90° F. In the second series, 6- by 12-inch cardboard cylinder molds were filled with concrete made at 73° F., sealed with a glass plate and heavy grease, and placed in a metal can 11 inches in diameter and 15 inches in height. Expanded mica was placed around all surfaces of the cylinder mold and on the glass plate, and the cans were stored in laboratory air maintained at a temperature of 73° F. Each cylinder was molded with a copper-constantan thermocouple at its symmetrical center and the temperatures were recorded on an eight-point potentiometer. The amount of each retarder used was that amount necessary for 2½ to 3 hours retardation at 73° or 90° F.

All cylinders for compressive strength tests were capped on both ends with high-alumina cement after removal from the molds, and at least 48 hours prior to testing. All caps were within 0.001 inch of planeness. The cylinders were loaded at a rate of 35 p.s.i. per second.

Beams for flexural strength were tested in accordance with AASHO method T 97. When bearings on beams did not meet the requirements for planeness, they were ground with a power driven carborundum wheel.

Beams measuring 3 by 4 by 16 inches were tested for resistance to freezing and thawing in accordance with the standard method of fast freezing and thawing in water, AASHO method T 161.

Measurements for volume change of 3- by 4- by 16-inch beams were made on a horizontal comparator with a micrometer dial reading to 0.0001 inch at 1 end and a micrometer barrel reading to 0.0001 inch at the other end. Beams were molded with stainless steel studs in the ends and stored with the 4-inch axis in a vertical position during the curing and drying period.

Tests for static modulus of elasticity were made on 6- by 12-inch cylinders at 7 and 28 days by an autographic stress-strain recorder with a 6-inch gage length. These tests were paralleled by sonic modulus of elasticity tests on 6- by 6- by 21-inch beams which were made from the same batch of concrete as the cylinders.

Density and absorption tests were made on 2 disks, each 1 inch in thickness, which were cut from the top, middle, and bottom of the 6- by 12-inch concrete cylinders. The cylinders were molded from mixes Nos. 1 and 2. The disks were cut by a diamond wheel at an age of 28 days from moist-cured cylinders and were weighed in air and under water. They were then dried to constant weight in a forced air oven at 190-200° F.

One procedure in the mixing and testing of the plastic concrete and the testing of hardened concrete should be emphasized. Every

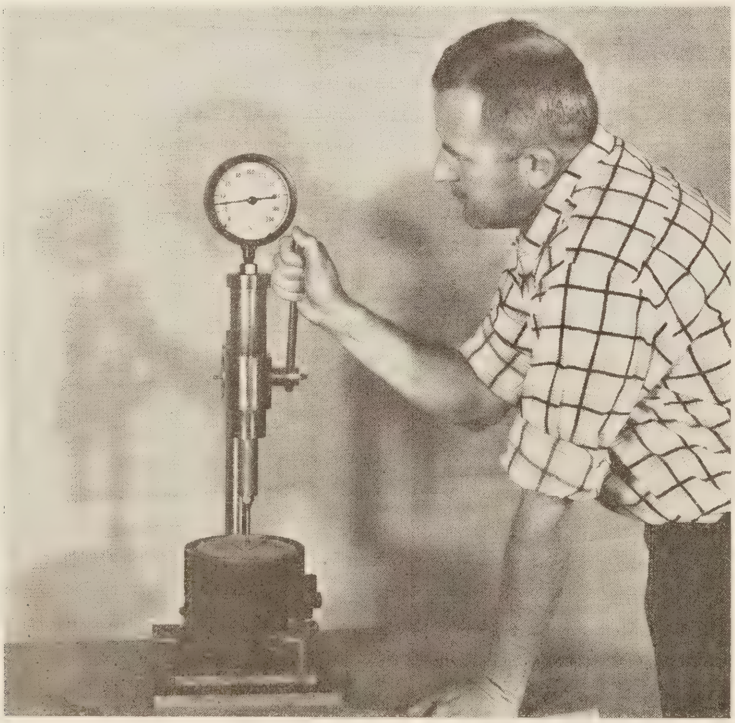

Figure 1.—Proctor penetration device.

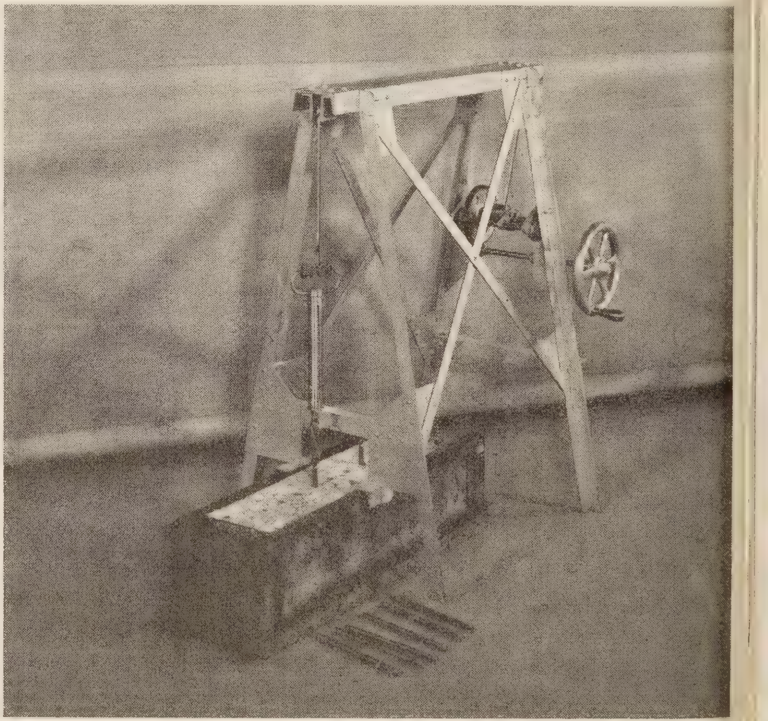

Figure 2.—Pin pullout device.

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[4] *Measuring the rate of hardening of concrete by bond pullout pins,* by T. M. Kelly and D. E. Bryant, ASTM Proceedings, vol. 57, 1957, pp. 1029–1042. This method is referred to as the pin pullout method.

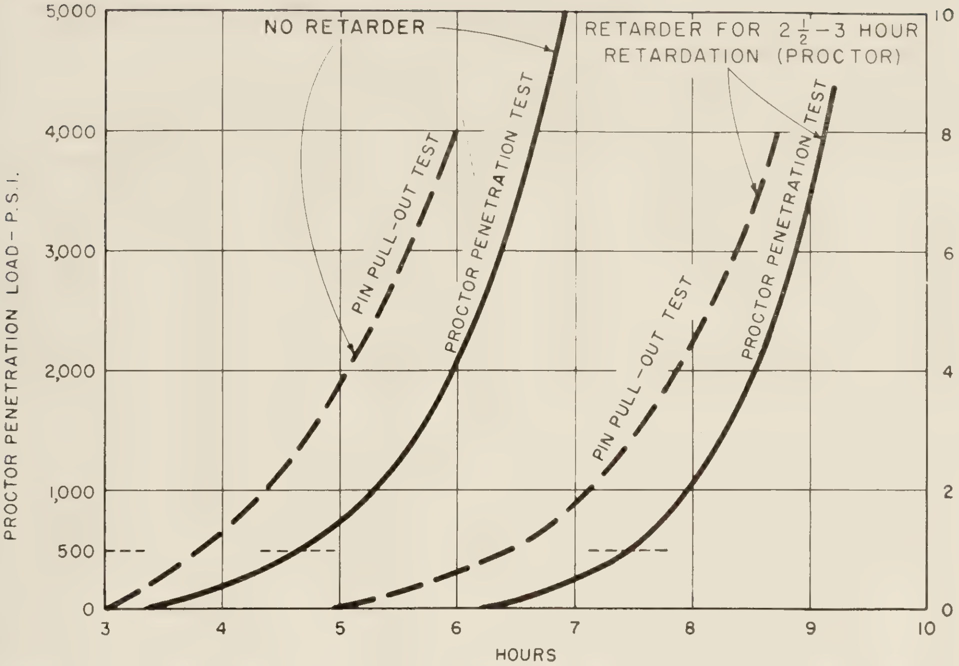

Figure 3.—Typical curve for Proctor penetration and pin pullout tests for retardation time on concrete.

test made on plastic or hardened concrete included specimens from mix No. 1, the reference mix without retarder.

Discussion of Test Results

The test data results are shown in tables 4–13, and in figures 4–12. The effect of retarders on the concrete are discussed in terms of the main objectives of the study, which were to determine the effect of the retarder on: (1) retardation of setting time, (2) water content and air-entrainment, (3) strength, (4) durability, and (5) volume change. Additional tests, such as the effect of overdosage of retarders, retardation and strength at elevated temperature, modulus of elasticity, delayed vibration, density and absorption, and temperature rise, are also discussed.

Effect of Admixtures on Time of Retardation

The amount of each retarder and the resulting retardation, as measured by the Proctor penetration test at 500 p.s.i. or 4,000 p.s.i. penetration pressure, or by the pin pullout test at 8 p.s.i. are shown in table 4. Each value is the average of 2 tests that were made on 2 days. Retardation is the difference in setting time between that for the reference mix (No. 1) and that for the concrete with the retarder (mix No. 2). Recommendations for the amount of retarder to be used were furnished by the manufacturers of 22 of the retarders included in these tests. For 13 retarders, the amount recommended was found to give the desired retardation of 2½ to 3 hours. For two retarders, 80 percent of the recommended amount was found to be sufficient, and for three other retarders, 120 to 125 percent of the recommended amount was needed. For the other 4 retarders, 150 to 500 percent of the recommended amount was required to obtain an effective amount of retardation. These 4 were retarders Nos. 2, 6, 22, and 23. Except for sample No. 6, these retarders were lignosulfonates.

The 500 p.s.i. penetration pressure of the Proctor test is believed to indicate the initial setting of the mortar used. At the initial setting, however, the mortar could still be remolded without injury to its strength. When determinations were made using a penetration pressure of 4,000 p.s.i., a condition at or near the final setting of the mortar was indicated. Attempts to rework the mortar at that time resulted in its disruption. In the pin pullout test, no attempt was made to define or determine the setting time of the concrete. Conducted under defined conditions, the test was intended to permit comparisons of the rates of hardening of different concretes. The comparison of typical retardation values for the Proctor penetration and pin pullout tests, shown in figure 3, indicated that a 500 p.s.i. penetration corresponds to a pin pullout load of 2½ to 2¾ p.s.i. However, the ranges of values shown in figure 4 indicated that for the concretes used in these tests, the Proctor penetration test with either of the loads used appeared to be more suitable for measuring setting time and retardation than the pin pullout test. The wide range of values for the pin pullout test and lack of a definite central point indicated that the test result probably was affected by uncontrolled variables to a greater extent than the Proctor penetration test.

Effect of Retarders in Concrete

Table 5 shows the amount of Vinsol resin solution (air entraining agent) used in concretes for mixes Nos. 2 and 3 for strength tests at 73° F. and the resulting water and air contents of the concrete. (The retarders generally were given their identification numbers in ascending order of the reduction in water requirements for mix No. 2. The exception is retarder No. 12 which is slightly out of place in the table.) The detailed data for the reference mix (No. 1) are not tabulated for results on each retarded concrete mix, but the average values for all reference mixes are given in a footnote. The values given in table 5 are averages of five rounds of tests.

The reduction in water content shown for mix No. 2 is the difference between the amount of water used for mix No. 1 and mix No. 2 made on the same day. This is shown as a percentage of the amount of water used for

(Continued on page 142)

Table 4.—Retardation time for concrete mix No. 2 at 73° F.[1]

Retarder No.	Amount retarder used	Air [2]	Slump	Proctor penetration test,[3] retardation at—		Pin pull-out test, retardation at 8 p.s.i.[4]
				500 p.s.i.[4]	4,000 p.s.i.[4]	
	Oz./bag	*Percent*	*Inches*	*Hr. Min.*	*Hr. Min.*	*Hr. Min.*
1	1.1	5.0	2.6	2:50	2:45	2:40
2	14.4	5.0	2.5	2:30	2:10	2:20
3	4.0	6.1	3.0	2:45	2:35	2:30
4	3.0	5.4	3.2	2:30	2:30	2:55
5	4.0	5.4	3.1	2:40	2:20	1:25
6	4.0	5.7	3.2	2:20	2:15	2:30
7	3.5	5.0	2.7	2:45	2:40	3:00
8	12.0	6.3	3.2	2:50	3:00	2:25
9	2.8	6.0	2.8	2:30	2:35	2:15
10	3.2	6.2	2.6	2:30	2:45	2:20
11	4.8	5.4	3.0	2:50	2:30	2:50
12	4.0	5.2	3.0	2:50	2:50	2:05
13	4.8	5.4	3.0	2:20	2:30	2:15
14	5.0	4.3	3.3	2:40	2:45	2:40
15	4.0	7.5	3.0	2:35	3:00	1:55
16	4.8	6.2	3.0	2:50	2:35	1:50
17	3.2	5.5	2.6	2:50	3:00	2:20
18	4.0	5.0	2.8	2:20	2:00	1:00
19	4.0	5.5	2.8	2:40	3:00	2:05
20	9.0	5.0	2.2	2:25	2:30	2:35
21	9.0	6.4	3.5	2:30	2:40	2:10
22	4.0	10.0	2.6	2:30	2:30	1:50
23	6.4	7.0	3.0	2:40	2:40	1:40
24	9.6	5.4	2.4	2:40	2:25	1:55
25	4.0	7.0	2.8	2:35	2:35	1:30

[1] Each value is an average of 2 tests made on different days.

[2] Neutralized vinsol resin solution used when needed.

[3] A load of 500 p.s.i. indicates the vibration limit of the concrete; a load of 4,000 p.s.i. indicates hardened concrete. Retardation is the delay in time of hardening of the concrete containing the retarders as compared with non-retarded concrete made on the same day.

[4] Time for nonretarded concrete to reach: Proctor penetration load of 500 p.s.i. is 5 hrs. 10 min. (±20 min.); Proctor penetration load of 4,000 p.s.i. is 7 hrs. 35 min. (±30 min.); pin pullout load of 8 p.s.i. is 6 hrs. 40 min. (±20 min.).

STATE LEGAL MAXIMUM LIMITS OF MOTOR VEHICLE

Prepared by the Bure

Line	State	Width inches[1]	Height ft.-in.	Length—feet[2]				Number of towed units[3]			Axle load—pounds				Gross
				Single unit		Truck tractor semi-trailer	Other combination	Semi-trailer	Full trailer	Semi-trailer and full trailer	Single		Tandem		Type of restriction
				Truck	Bus						Statutory limit	Including statutory enforcement tolerance	Statutory limit	Including statutory enforcement tolerance	
1	Alabama	96	[6] 12-6	35	40	50	NP	1	NP	NP	18,000	19,800	36,000	39,600	Table
2	Alaska	96	12-6	35	[19] 40	60	60	1	1	2	18,000		32,000		Table-tire cap.
3	Arizona	96	13-6	40	40	65	65	1	1	2	18,000		32,000		Table
4	Arkansas	96	13-6	35	40	50	50	1	1	NP	18,000	[7] 18,500	32,000	32,500	Spec. maximum[8]
5	California	96	13-6	35	[9] 35	60	65	NR	NR	NR	18,000		32,000		Table
6	Colorado	[11] 96	[12] 13-6	35	40	60	60	1	2	2	18,000		36,000		Formula-spec. limits
7	Connecticut	102	12-6	50	50	50	NP	1	NP	NP	22,400	22,848	36,000	36,720	Spec. lim.-tire cap.
8	Delaware	96	[6] 12-6	40	42	50	60	1	1	2	20,000		36,000		Table-spec. limits[13]
9	District of Columbia	96	12-6	35	35	50	80	1	1	NP	22,000		38,000		Table
10	Florida	96	[6] 12-6	[14] 35	40	50	50	1	1	NP	20,000	22,000	40,000	44,000	Table
11	Georgia	96	13-6	[15] +39	[15] +45	50	50	1	1	NP	18,000	20,340	36,000	40,680	Spec. maximum[16]
12	Hawaii	108	13-0	40	40	55	65	1	1	2	24,000		32,000		Formula[17]
13	Idaho	[18] 96	14-0	35	[19] 40	60	65	1	1	2	[20] 18,000		[20] 32,000		Table[20]
14	Illinois	96	13-6	42	42	50	50	1	1	2	[21] 18,000		32,000		Spec. lim.-tire cap.
15	Indiana	96	13-6	36	40	50	50	1	1	2	[23] 18,000	[23] 19,000	[23] 32,000	[23] 33,000	Spec. lim.-tire cap.
16	Iowa	96	13-6	35	[19] 40	50	NP	1	[24] 1	NP	18,000	18,540	32,000	32,960	Table
17	Kansas	96	13-6	35	[19] 40	50	50	1	1	NP	18,000		32,000		Table
18	Kentucky	96	[25] 13-6	[26] 35	[26] 35	[27] 50	NP	1	NP	NP	18,000	[28] 18,900	32,000	[28] 33,600	Spec. lim.-tire cap.[29]
19	Louisiana	96	13-6	35	[19] 40	50	60	1	1	NP	18,000		32,000		Axle lim.-tire cap.
20	Maine	96	[30] 12-6	50	50	50	50	1	1	NP	[30] 22,000		[30] 32,000		Table-tire cap.
21	Maryland	96	[6, 45] 12-6	55	55	55	55	NR	NR	NR	22,400		40,000		Formula
22	Massachusetts	96	NR	35	[19] 40	[31] 50	NP	1	NP	NP	22,400		36,000		Table-spec. limits
23	Michigan	96	13-6	35	40	55	55	1	1	2	[33] 18,000		[34] 32,000		Axle lim.-tire cap.
24	Minnesota	96	13-6	40	40	50	50	1	1	NP	18,000		32,000		Table
25	Mississippi	96	[6] 12-6	35	40	[36] 50	50	1	1	NP	18,000		28,650	[35] 32,000	Table-tire cap.
26	Missouri	96	12-6	35	40	50	50	1	1	2	18,000		32,000		Table
27	Montana	[18] 96	13-6	35	40	60	60	1	1	[37] 2	18,000		32,000		Table
28	Nebraska	96	13-6	40	40	60	60	1	1	2	18,000	18,900	32,000	33,600	Table
29	Nevada	96	NR	NR	NR	NR	NR	NR	NR	NR	18,000	18,900	32,000	33,600	Table
30	New Hampshire	96	13-6	35	[38] 40	50	50	NR	NR	NR	22,400		36,000		Tables-spec. limits
31	New Jersey	96	13-6	35	[39] 35	50	[40] 50	1	1	NP	22,400	23,520	32,000	33,600	Spec. limits
32	New Mexico	[41] 96	13-6	40	40	65	65	1	1	2	21,600		34,320		Table
33	New York	96	13-0	35	[42] 35	50	50	1	1	NP	22,400		36,000		Formula
34	North Carolina	96	[6] 12-6	35	[19] 40	[43] 50	[43] 55	1	1	NP	18,000	19,000	36,000	38,000	Spec. limits
35	North Dakota	96	13-6	[14] 35	[19] 40	60	60	1	1	2	18,000		32,000		Formula
36	Ohio	96	13-6	35	[19] 40	50	60	1	NR	NR	19,000		31,500		Formula
37	Oklahoma	96	13-6	35	45	50	50	1	1	NP	18.000		32,000		Table
37	Oregon	96	[45] 13-6	35	[35] 40	[46, 35] 55	[35] 65	1	1	[35] 2	[47] 18,000		[47] 32,000		Table[48]
38	Pennsylvania	96	[6] 12-6	35	[19] 40	50	[40] 50	1	1	NP	22,400	23,072	36,000	37,080	Spec. limits[49]
39	Puerto Rico	96	12-6	35	35	50	50	1	1	NP	NS		NS		Spec. lim.-tire cap.[63]
40	Rhode Island	102	12-6	40	40	50	50	1	1	NP	22,400		NS		Spec. limits
42	South Carolina	96	13-6	[14] 35	[19] 40	55	60	1	1	NP	20,000		32,000		Table
43	South Dakota	96	13-0	35	40	50	60	1	1	2	18,000		32,000		Table
44	Tennessee	96	[6] 12-6	35	40	50	50	1	[53] 1	NP	18,000		32,000		Table
45	Texas	96	13-6	35	40	50	50	1	1	NP	18,000	18,900	32,000	33,600	Table
46	Utah	96	14-0	45	45	60	60	NR	NR	NR	18,000		33,000		Table
47	Vermont	96	12-6	50	50	50	50	1	1	NP	NS		NS		Spec. lim.-tire cap.
48	Virginia	96	[6] 12-6	35	[35] 40	50	50	1	1	NP	18,000		[57] 32,000		Table
49	Washington	96	13-6	35	[19] 40	60	[58] 65	1	1	[58] 2	18,000	[59] 18,500	32,000	[59] 33,000	Table-spec. lim[59]
50	West Virginia	96	[6] 12-6	35	[19] 40	50	50	1	1	NP	18,000	18,900	32,000	33,600	Table
51	Wisconsin	96	13-6	35	40	50	50	1	1	NP	18,000	[60] 19,500	30,400	32,000	Table-formula[61]
52	Wyoming	96	13-6	40	40	60	60	1	1	2	18,000		32,000	[62] 36,000	Table
	AASHO Policy	96	12-6	35	[19] 40	50	60	1	1	NP	18,000		32,000		Table
Number of States	Higher	3	33	17	28	18	9	5	7	24	31		30		Formula 6
	Same	49	19	35	19	34	12	47	41	28	21		21		Table 32
	Lower	0	0	0	5	0	31	0	4	0	0		1		Specified limits 14

NP—Not permitted. NR—Not restricted. NS—Not specified.

[1] Various exceptions for farm and construction equipment; public utility vehicles; house trailers; urban, suburban, and school buses; haulage of agricultural and forest products; at wheels of vehicles; for safety accessories, on designated highways, and as administratively authorized.

[2] Various exceptions for utility vehicles and loads, house trailers and mobile homes.

[3] When not specified, limited to number possible in practical combinations within permitted length limits; various exceptions for farm tractors, mobile homes, etc.

[4] Legally specified or established by administrative regulation.

[5] Computed under the following conditions to permit comparison on a uniform basis between States with different types of regulation:

A. Front axle load of 8,000 pounds.

B. Maximum practical wheelbase within applicable length limits:

(1) Minimum front overhang of 3 feet.

(2) In the case of a 4-axle truck-tractor semitrailer, rear overhang computed as necessary to distribute the maximum possible uniform load on the maximum permitted length of semitrailer to the single drive-axle of the tractor and to the tandem axles of the semitrailer, within the permitted load limits of each.

(3) In the case of a combination having 5 or more axles, minimum possible combined front and rear overhang assumed to be 5 feet, with maximum practical load on maximum permitted length of semitrailer, subject to control of loading on axle groups and on total wheelbase as applicable.

C. Including statutory enforcement tolerances as applicable.

[6] Auto transports 13 feet 6 inches.

[7] Does not apply to combinations of adjacent load-carrying single axles.

[8] 56,000 pounds on load-carrying axles, exclusive of steering-axle load.

[9] On specific routes in urban or suburban service under special permit from P.U.C. 40 feet, also 3-axle buses with turning radius less than 45 feet without restriction.

[10] Effective September 18, 1959 on Interstate, 4-lane, and designated State highways.

[11] Buses 102 inches.

[12] On designated highways; 12 feet 6 inches on other highways.

[13] Legal limit 60,000 pounds, axle spacing 27 feet or more.

[14] Three-axle vehicles 40 feet.

[15] Truck 39.55 feet; bus 45.20 feet.

[16] 63,280 pounds maximum, except on roads under Rural Ro

[17] 700 (L+40) when L is 18' or less; 800 (L+40) when L is with span of 20' or over.

[18] Buses 102 inches on highways of surfaced width at leas

[19] Less than three axles 35 feet.

[20] Special limits for vehicles hauling timber and timber pro including livestock; single axle 18,900 pounds, tandem axle 3 mitted 66,000 pounds maximum at 21-foot axle spacing, vehicl foot axle spacing.

[21] On designated highways; 16,000 pounds on other highwa

[22] Without tandem axles 45,000 pounds.

[23] On designated highways; single axle 22,400 pounds, tan excesses of weight under one or more limitations of axle load

[24] Limited to 4 wheel trailer towed by truck not exceeding

[25] Class AA highways; 12 feet 6 inches on other highways

[26] On designated highways; trucks 26.5 feet and buses 30

[27] Class AA highways; 45 feet on other highways.

[28] Class AA highways only.

[29] Maximum gross weight on Class A highways 42,000 pour

[30] Including load 14 feet; various exceptions for vehicles

[31] Effective September 21, 1959.

[32] Subject to axle and tabular limits.

[33] Single axle spaced less than 9 feet from nearest axle li

[34] On designated highways only and limited to one tandem

[35] On designated highways only (by permit in Oregon).

[36] Auto transports permitted 50 feet.

[37] Semitrailer and semitrailer converted to full trailer by m

ND WEIGHTS COMPARED WITH AASHO STANDARDS

Roads, July 1, 1960

			Specified maximum gross weight—pounds[4]						Practical maximum gross weight—pounds[5]						Line
	Applicable to:		Truck		Truck-tractor semitrailer			Other combination	Truck		Truck-tractor semitrailer			Other combination	
	Any group of axles	Total wheel base only	2-axle	3-axle	3-axle	4-axle	5-axle		2-axle	3-axle	3-axle	4-axle	5-axle		
		X							27 800	47,600	47,600	60,010	64,650	NP	1
	Under 18'	Over 18'	29,000	43,000	47,000	61,000	75,000	75,000	26,000	40,000	44,000	58,000	72,000	75,000	2
	under 18'	Over 18'							26,000	40,000	44,000	58,000	72,000	76,800	3
									26,500	40,500	45,000	59,000	65,000	65,000	4
	Under 18'	Over 18'							26,000	40,000	44,000	58,000	72,000	76,000	5
+40)		X	30,000	46,000					26,000	44,000	44,000	62,000	76,000	76,000	6
			32,000	50,000	50,000	60,000	60,000	NP	30,848	44,720	51,000	61,200	61,200	NP	7
	X		30,000	46,000	48,000	60,000	60,000	60,000	28,000	48,000	48,000	56,350	60,000	60,000	8
	X								30,000	46,000	52,000	[54] 58,450	[54] 61,490	[54] 64,650	9
		X							30,000	52,000	52,000	65,200	73,095	73,095	10
								63,280	28,340	48,680	48,680	63,280	63,280	63,280	11
	X								32,000	38,800	56,000	64,000	72,000	80,000	12
	X								26,000	40,000	44,000	58,000	72,000	76,800	13
			36,000	[22] 41,000	45,000	59,000	72,000	72,000	26,000	40,000	44,000	58,000	72,000	72,000	14
								72,000	27,000	41,000	45,000	59,000	[23] 73,000	[23] 73,000	15
	X								26,540	40,960	45,080	59,500	73,280	NP	16
	X								26,000	40,000	44,000	55,470	63,890	63,890	17
			36,000	50,000	54,000	59,640	73,280	NP	26,900	41,600	45,800	59,640	73,280	NP	18
									26,000	40,000	44,000	58,000	72,000	76,000	19
	X		32,000	[30] 50,000	50,000	60,000	60,000	60,000	30,000	40,000	50,000	60,000	60,000	60,000	20
+40)		X			65,000	65,000	65,000	65,000	30,400	48,000	52,800	65,000	65,000	65,000	21
+25)		X	[32] 46,000	[32] 60,000	[32] 60,000	[32] 60,000	[32] 60,000	NP	30,400	44,000	52,800	60,000	60,000	NP	22
									26,000	[35] 40,000	44,000	[35] 58,000	[35] 66,000	[35] 102,000	23
	X								26,000	40,000	44,000	58,000	68,000	72,500	24
	X								26,000	[35] 40,000	44,000	59,000	[35] 64,650	[35] 64,650	25
	X								26,000	40,000	44,000	55,470	64,650	64,650	26
	Under 18'	Over 18'							26,000	40,000	44,000	58,000	72,000	76,000	27
	X		36,000	54,000	54,000	71,146	71,146	71,146	26,780	41,200	45,320	59,740	73,280	73,280	28
	Under 18'	Over 18'							26,900	41,600	45,800	60,500	75,200	76,800	29
		X	33,400	[38] 47,500	52,800	66,400			30,400	44,000	52,800	66,400	66,400	66,400	30
			30,000	40,000	60,000	60,000	60,000	60,000	31,500	41,600	55,040	63,000	63,000	63,000	31
	Under 18'	Over 18'							29,600	42,320	51,200	63,920	76,640	86,400	32
50 L		X					65,000	65,000	30,400	44,000	52,800	65,000	65,000	65,000	33
			31,500	46,200	46,200	65,100	65,100	65,100	27,000	46,000	46,000	65,100	65,100	65,100	34
+40)	Under 18'	Over 18'							26,000	38,000	44,000	56,000	[44] 64,000	[44] 64,000	35
00L		X							27,000	39,500	46,000	58,500	71,000	78,000	36
	X								26,000	40,000	44,000	58,000	72,000	73,280	37
	Under 18'	Over 18'					[48] 74,000	[48] 76,000	26,000	40,000	44,000	58,000	[48] 72,000	[48] 76,000	38
			33,000	47,000	50,000	60,000	60,000	62,000	31,072	45,080	51,500	61,800	61,800	63,860	39
															40
			[50] 36,000	[51] 44,000	[52] 50,000	[13] 60,000	60,000	88,000	30,400	44,000	50,000	60,000	60,000	88,000	41
	X								28,000	40,000	48,000	60,000	66,839	71,115	42
	X								26,000	40,000	44,000	58,000	72,000	73,280	43
		X							26,000	40,000	44,000	58,000	61,580	43,500	44
	X								26,900	41,600	45,800	60,500	75,200	75,600	45
	Under 18'	Over 18'							26,000	41,000	44,000	59,000	74,000	79,900	46
			30,000	[55] 50,000	50,000	[56] 60,000	[56] 60,000	[56] 60,000	30,000	[55] 50,000	50,000	60,000	60,000	60,000	47
	X						[35] 56,800	[35] 56,800	26,000	40,000	44,000	56,800	56,800	56,800	48
	Under 18'	Over 18'	28,000	36,000	46,000	60,000	68,000	72,000	26,000	36,000	44,000	60,000	68,000	72,000	49
	X								26,900	41,600	45,800	57,844	63,840	63,840	50
.+26)	X								27,500	40,000	47,000	59,500	73,000	73,000	51
	X								26,000	44,000	44,000	62,000	73,950	73,950	52
-3L[2]	X								26,000	40,000	44,000	55,470	61,490	71,900	
	19	19							29 22 0	27 20 4	29 22 0	48 3 0	42 2 7	26 0 25	

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y 56,000 pounds maximum.

18'; 900 (L +40) on highways having no structures

otherwise as administratively authorized.

concentrates, aggregates, and agricultural products

, gross weight table: vehicle with 3 or 4 axles per-

ore axles permitted 79,000 pounds maximum at 43-

,000 pounds; tolerance of 1,000 pounds on total of all

eight.

ss weight.

highways.

s B highways 30,000 pounds.

t products and construction materials.

00 pounds.

ination; otherwise 26,000 pounds.

lly.

[38] Dual-drive axles; otherwise 40,000 pounds.

[39] Or as prescribed by P.U.C.

[40] Exception for poles, pilings, structural units, etc., permitted 70 feet.

[41] On designated highways 102 inches.

[42] Trackless trolleys and buses 7 passengers or more, P.S.C. certificate 40 feet.

[43] Including front and rear bumpers.

[44] Approved equipment 73,280 pounds.

[45] Certain types of vehicles and commodities under annual permits on designated highways up to 13 feet 6 inches

[46] 60 feet allowed truck tractor semitrailer on major routes designated by permit.

[47] Logging vehicles permitted 3-foot wheelbase tolerance, 19,000-pound single axle, 34,000-pound tandem axle.

[48] Governs gross weight permitted on highways designated by resolution of State highway commission or by permit.

[49] Single unit truck with 4 axles permitted 60,000 pounds.

[50] Axles spaced less than 6 feet 32,000 pounds; less than 12 feet 36,000 pounds; 12 feet or more gross weight governed by axle limit.

[51] Single vehicle with 3 or more axles spaced less than 16 feet 40,000 pounds; less than 20 feet 44,000 pounds; 20 feet or more governed by axle limit.

[52] Tractor semitrailer with 3 or more axles spaced less than 22 feet 46,000 pounds; not less than 27 feet 50,000 pounds.

[53] Limited to 3,500 pounds.

[54] Pavements only, maximum legal load for bridges 56,800 pounds.

[55] On Interstate routes 40,000 pounds.

[56] Tandem axles on trailer equipped with adequate brakes.

[57] Vehicles registered before July 1, 1956, permitted limits in effect January 1, 1956, for life of vehicle.

[58] Three-unit combinations on designated highways.

[59] Vehicles hauling logs permitted wheelbase and gross weight tolerances. Discretionary enforcement tolerances not included in computation of practical maximum gross weights.

[60] Axle load 21,000 pounds on 2-axle trucks hauling peeled or unpeeled forest products cut crosswise.

[61] On Class A and Class B highways. All axles of a vehicle or combination—73,800 pounds maximum.

[62] Based on ruling of Attorney General.

[63] Dimensional limits effective August 20, 1960; weight limits to be established by administrative regulations.

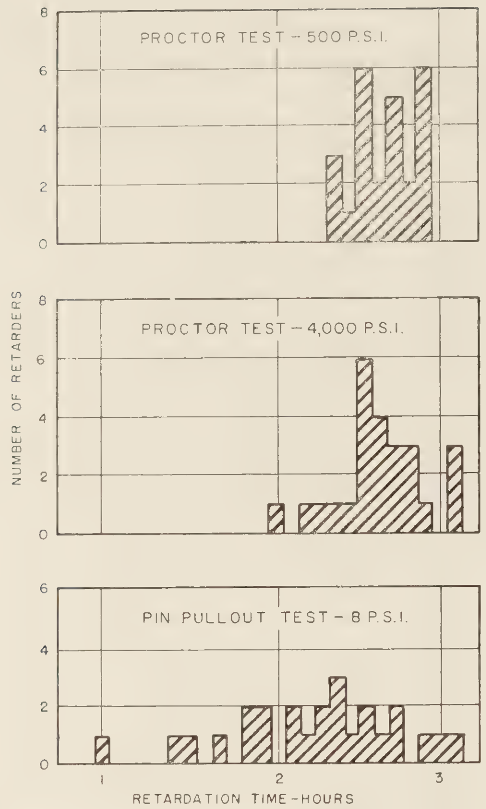

Figure 4.—Time distribution of retardation.

(Continued from page 139)

mix No. 1. A comparison between this reduction in water content and the amount of retarder used for mix No. 2 is shown in figure 5. It was noted that some retarders were much more effective in permitting a reduction in the amount of water required to obtain concrete of a given slump. A comparison between the amount of reduction in water and the amount of retarder used per bag of cement showed that retarder No. 25 was the most effective and retarder No. 2 was the least effective. These retarders reduced the water required for mix No. 2 by 2.9 percent and 0.2 percent, respectively, per ounce of retarder used per bag of cement. The amount of volatile organic material used is shown in table 1 and figure 5. For the lignosulfonates this amount was between two and four ounces per bag except for retarders Nos. 2 and 24. Of the 9 most effective retarders with respect to reduction in water, all were lignosulfonates except for 1 organic acid.

Water content

The concretes of mix No. 3 were prepared with cement contents reduced in accordance with the amount of reduction in water found possible for mix No. 2, the objective being to have the same water content in mix No. 3 as in mix No. 1. For retarders which permitted a reduction in water of 5 percent or less in mix No. 2, the cement content for mix No. 3 was reduced 0.25 bag per cubic yard. (This is designated as group A in table 3.) For retarders which permitted a reduction of water of over 5 percent but less than 10 percent, the cement content for mix No. 3 was reduced 0.5 bag per cubic yard (group B in table 3). For retarders permitting a reduction in water of 10 percent or more, the cement content was reduced 0.75 bag per cubic yard (group C). It was found that, due to uncontrollable variables, it was not possible to prepare all batches of concrete with these exact cement contents, and at the same time maintain a slump of 2.8 ± 0.3 inches and use the same amount of water in mix No. 3 as was used in the reference mix. To hold the cement content and slump as close as possible to the desired values, slight variations in the water content were permitted. For 18 of the 25 retarders, the water contents were within 0.1 gallon per bag of cement of the desired values, and in only one case (sample No. 23) did the actual water content and the desired content differ by more than 0.2 gallon per bag. In view of these small differences, mix No. 3 was considered to have the same water content as the reference mix.

Air entraining agent

The amount of Vinsol resin solution required to entrain 5 to 6 percent air in the mix No. 2 concrete prepared with an organic acid retarder (Nos. 4, 5, 6, 8, or 9) was approximately two-thirds of that used in the reference mix. The water reduction caused by the five organic acid retarders varied from 5.3 to 6.6 percent. The amount of air-entraining solution used in the mix No. 3 concrete with a decreased cement content of ¼ to ¾ of a bag per cubic yard was approximately the same as the quantity needed for mix No. 2. Although experience has shown that the organic acid retarders cause no air entrainment in concrete, these data indicate that they aid air entrainment and permit a moderate reduction in water content when used at the rate of 2.8 to 12 ounces per bag of cement.

The concrete prepared with each of the lignosulfonate retarders showed a wide range, 2.8 to 11.8 percent, in water reduction. The reduction of 2.8 percent was obtained by use of a powdered lignosulfonate which contained over 95 percent of an inorganic filler. Two lignosulfonates permitted reductions of 5.2 and 5.9 percent, respectively; 12 permitted reductions of 7 to 10 percent; and 4 permitted reductions of 10 to 12 percent. It should be noted that in retarder samples Nos. 1 and 2, although the water reduction for concrete was lower than is usually specified, satisfactory retardation was obtained.

Air content

The effect of each of the 25 retarders on air content of concrete and the amount of air-entraining admixture used is shown in figure 6.

Table 5.—Mix data for strength tests [1]

Retarder No.	Water for mix No. 1 [2]	Mix No. 2—same cement content as mix No. 1						Mix No. 3—same water content as mix No. 1				
		AEA added	Cement	Slump	Air	Water	Reduction in water [3]	AEA added	Cement	Slump	Air	Water
	Gal./bag	*Ml./bag*	*Bags/cu. yd.*	*Inches*	*Percent*	*Gal./bag*	*Percent*	*Ml./bag*	*Bags/cu. yd.*	*Inches*	*Percent*	*Gal./bag*
1	5.75	17.1	6.0	2.8	5.0	5.69	1.1	19.0	5.7	2.7	5.6	5.89
2	5.77	16.2	6.0	2.6	5.2	5.61	2.8	18.0	5.7	2.9	5.6	5.93
3	5.79	--------	6.0	3.1	5.9	5.49	5.2	--------	5.5	2.8	5.6	5.89
4	5.81	13.7	6.0	2.9	5.7	5.50	5.3	14.5	5.4	2.8	5.8	6.01
5	5.74	11.5	6.0	3.1	5.5	5.41	5.7	12.3	5.5	2.7	5.8	5.81
6	5.87	15.1	6.0	2.7	5.4	5.53	5.8	16.4	5.5	2.9	5.9	6.03
7	5.76	8.3	6.0	2.7	5.4	5.42	5.9	9.2	5.5	2.6	5.5	5.84
8	5.78	15.8	6.0	2.6	5.5	5.43	6.1	14.7	5.5	2.8	5.6	5.88
9	5.91	14.5	6.0	2.9	5.2	5.52	6.6	16.6	5.5	2.6	5.7	6.04
10	5.86	9.4	6.0	3.0	5.4	5.44	7.2	8.6	5.6	2.7	5.1	5.76
11	5.71	3.7	6.0	2.7	5.7	5.29	7.4	4.1	5.5	2.7	5.5	5.71
12	5.86	2.5	6.0	2.6	5.4	5.37	8.4	--------	5.5	2.7	5.6	5.87
13	5.77	2.6	6.0	2.7	5.7	5.30	8.1	1.3	5.5	2.6	5.7	5.75
14	5.67	2.2	6.0	3.0	5.7	5.21	8.1	2.8	5.5	2.7	5.8	5.72
15	5.73	--------	6.0	3.0	6.8	5.26	8.2	--------	5.5	2.8	7.0	5.67
16	5.67	4.4	6.0	2.9	6.1	5.20	8.3	3.7	5.5	2.8	5.8	5.74
17	5.79	11.5	6.0	2.8	5.5	5.31	8.3	11.3	5.5	2.9	5.5	5.81
18	5.77	4.5	6.0	2.7	5.6	5.27	8.7	4.4	5.5	2.6	5.7	5.75
19	5.74	7.2	6.0	2.5	5.7	5.24	8.7	6.4	5.5	2.6	5.4	5.78
20	5.86	--------	6.0	2.8	5.3	5.30	9.6	1.8	5.5	2.6	5.5	5.81
21	5.84	4.0	6.0	2.7	5.7	5.27	9.8	2.8	5.5	2.6	5.7	5.72
22	5.80	--------	6.0	3.2	10.0	5.22	10.0	--------	5.2	3.1	10.0	5.88
23	5.75	--------	6.1	2.6	5.8	5.15	10.4	--------	5.3	2.6	5.4	6.03
24	5.78	--------	6.0	2.6	5.9	5.13	11.2	--------	5.2	2.6	5.8	5.86
25	5.76	--------	6.0	2.8	7.6	5.08	11.8	--------	5.2	2.8	9.5	5.72

[1] Each value is an average of five tests made on different days. Amount of retarder used is the same amount as shown in table 4.

[2] Water content for mix No. 1 is water used in reference mix made on same day as retarded concrete mixes. Average values for mix No. 1 are: air-entraining agent (AEA) added, 20 ml./bag; cement, 6.0 bags/ cu. yd.; slump, 2.9 inches; air, 5.4 percent.

[3] Average reduction in water-cement ratio as compared with that required for the reference mix made on the same day.

Seven of the 19 lignosulfonate retarders, without the use of an air-entraining solution, entrained more than 5 percent of air in the concrete. Three of these retarders caused air content of about 6 percent, while the maximum air content, 10 percent calculated gravimetrically, was obtained for the concrete containing retarder No. 22.

The amount of air entraining solution needed with each of the other 12 lignosulfonates to entrain 5 to 6 percent air in concrete mix No. 2 varied from about ⅛ to ½ of the quantity used in the reference mix, except in the case of retarder No. 2. The powdered extender and the small amount of lignosulfonate in this retarder probably accounted for the larger quantity of air-entraining solution required.

Retarder No. 1, sucrose of the carbohydrate group, caused a small reduction (1.1 percent) in water content and required almost as much air-entraining solution as the reference mix.

Effect of Admixtures on Strength of Concrete

Compressive strength test results

The results of the compressive strength tests on concrete containing the 25 retarders are given in table 6. Shown are the averages of five compressive strength tests for mixes Nos. 2 and 3 on 6- by 12-inch cylinders made on different days and tested at 3, 7, 28, and 365 days, and the ratios of these strengths to the average strengths of concrete without retarder (mix No. 1) made and tested on the same day as the concrete containing the retarder.

Average values for the compressive strength of all concretes prepared with and without the retarders are shown in figure 7. The curves show that both mix No. 2, with a reduced water content, and mix No. 3, with a reduced cement content, furnished higher average compressive strengths at all ages than was obtained without the use of retarders. This increase in compressive strength might be considered a secondary benefit obtained by the use of retarders, but it was a real and definite improvement in the characteristics of concrete.

As shown in table 6, all retarders except Nos. 22 and 25 furnished concrete of equal or higher strength at all ages than was obtained in the nonretarded concrete. Retarder No. 22 caused the entrainment of an excessive amount of air, and the strength suffered accordingly. Retarder No. 25 gave good results when used in mix No. 2 with a reduced water content. However, when used in mix No. 3 where the cement content was reduced, the concrete containing this retarder had lower strengths at all ages than the reference concrete. Retarder No. 25 also caused the entrainment of an excessive amount of air in mix No. 3. Study of the strengths obtained at all ages failed to show that any type of retarder gave better results than any other type.

Flexural strength test results

The results of the flexural strength tests for mixes Nos. 2 and 3 are given in table 7. This table gives the average of five tests on the 6- by 6- by 21-inch beams made on different days and tested at ages of 7 and 28 days. The ratios of these strengths to the strengths of concrete without retarder (mix No. 1) made and tested on the same day as the concrete containing the retarders are also given.

For some reason which was not apparent, the use of retarders failed to improve the flexural strength of concrete to the same extent as was found for the compressive strength. In the compression tests, the average strength of the reference mix concrete was 5,040 p.s.i. at an age of 28 days. The average strength of mix No. 2 retarded concrete was 115 percent of this, and that for mix No. 3 was 104 percent. In the tests for flexural strength, the reference concrete had

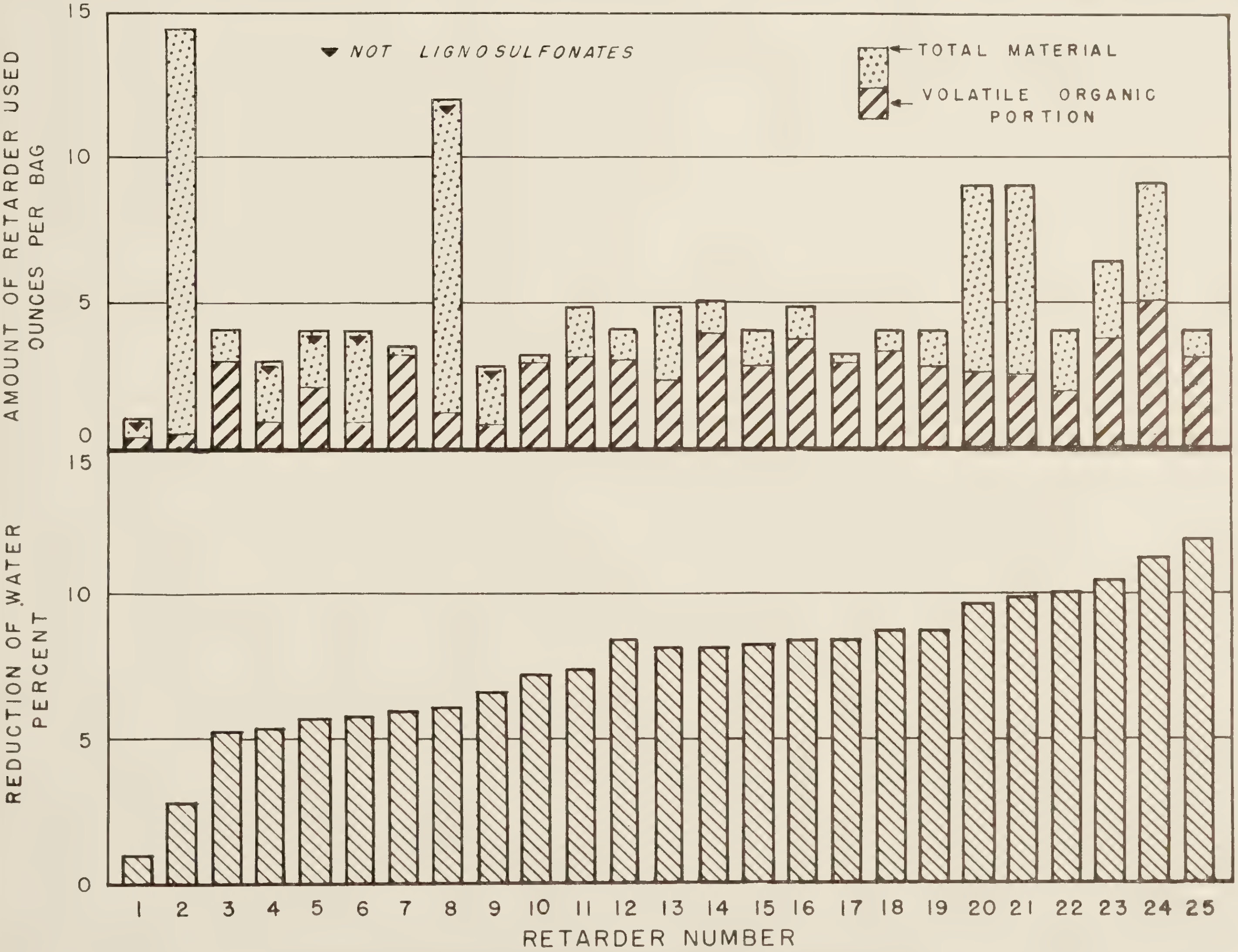

Figure 5.—Amount of retarder used and effect on water content.

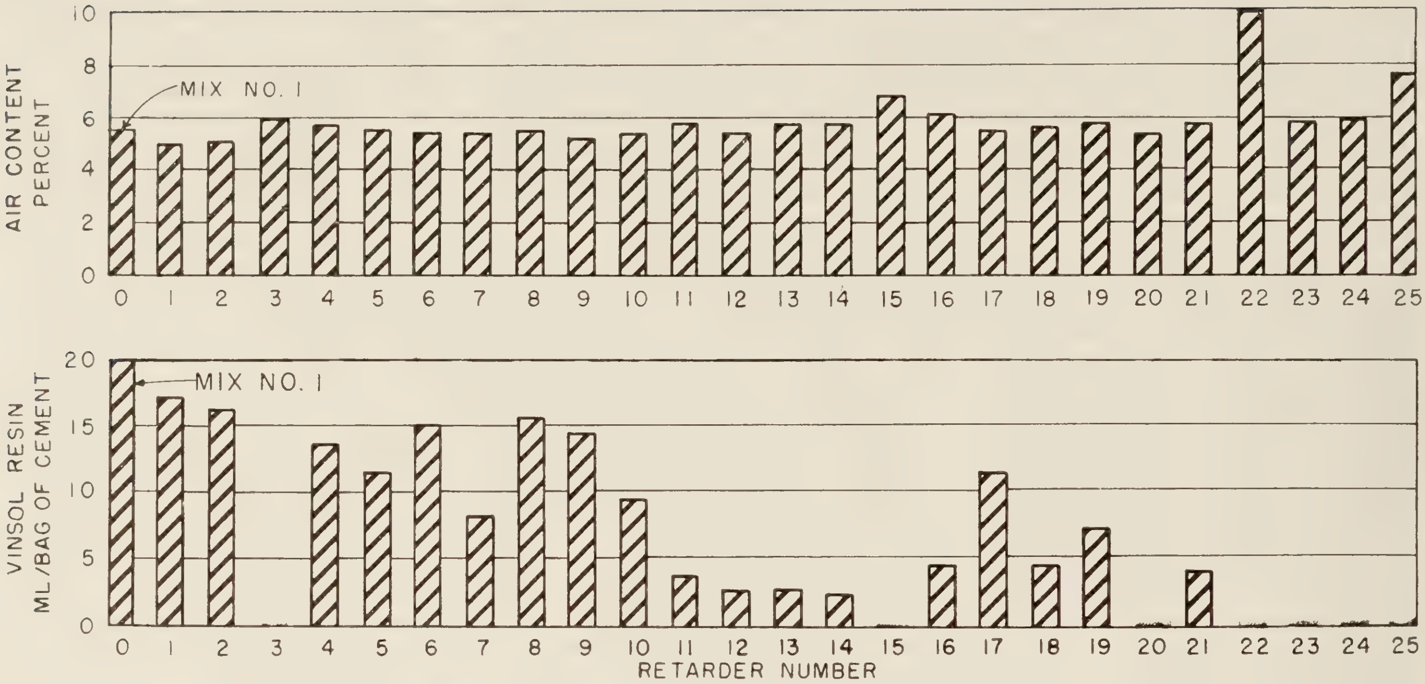

Figure 6.—Effect of retarder on air content of mix No. 2.

an average strength of 740 p.s.i. after 28 days, and mixes 2 and 3 of retarded concretes had average strengths of 104 and 97 percent, respectively, of the reference mix strength. It will be noted, however, that the ratio of the values of mixes Nos. 2 and 3 for compressive strength, 115 against 104, was practically the same as the ratio of values for flexural strength, 104 against 97. Consequently, it can be assumed that the results of the two sets of strength tests were valid and that the use of a retarder furnished concrete of lower relative flexural strength than compressive strength.

Studies of the different groups of retarders show that concretes prepared with the calcium lignosulfonate retarder had lower flexural strength than those prepared with the carbohydrate, the ammonium and sodium lignosulfonates, and the organic acids. No explanation can be given for this, nor for the behavior of concrete prepared with retarder No. 22. In the compression tests, concrete containing this retarder had the lowest strength, most likely due to the large amount of air entrained. In the flexural tests, this concrete had strengths lower than those of the reference concrete but with respect to the other retarded concretes, the strengths were reduced but slightly. It appears probable that in the acceptance testing of retarders, consideration should be given to the behavior of individual retarders and not assume that all retarders of a given type will affect concrete in the same manner.

In figure 8, average values of the effect of all retarders on the flexural strength of concrete are shown. These data are taken from two sets of specimens. The tests at ages of 7 and 28 days were made on 6- by 6- by 21-inch beams and the results obtained are shown in table 7. When these results were studied, it was observed that at an age of 28 days the average strength for the reference mix was greater than that for mix No. 3, and was approaching the strength for mix No. 2. A determination of the relative strengths of these concretes at greater ages was believed desirable.

As no other beams of 6- by 6-inch cross section were available, plans were made to test for flexural strength by using the 3- by

Table 6.—Compressive strength tests [1]

Retarder No.	Compressive strength for mix No. 2 [2]								Compressive strength for mix No. 3 [2]							
	3 days		7 days		28 days		1 year		3 days		7 days		28 days		1 year	
	P.s.i.	Ratio	P.s.i.	Ratio	P.s.i.	Ratio	P.s.i.	Ratio	P.s.i.	Ratio	P.s.i.	Ratio	P.s.i.	Ratio	P.s.i.	Ratio
1	2,910	126	4,210	118	5,700	115	6,890	114	2,700	117	3,950	111	5,450	110	6,510	107
2	2,910	123	3,980	110	5,370	108	6,520	109	2,620	111	3,840	106	5,090	102	6,070	102
3	2,910	125	3,990	116	5,240	110	6,400	113	2,430	105	3,460	100	5,030	106	6,050	107
4	2,930	126	4,430	125	5,900	120	6,890	117	2,410	103	3,970	112	5,180	105	6,180	105
5	3,260	132	4,600	124	6.090	120	7,080	115	2,920	119	4,120	111	5,580	110	6,590	108
6	2,910	126	4,290	124	5,610	118	6,740	118	2,480	107	3,800	110	5,160	109	6,130	107
7	3,030	122	4,310	118	5,720	114	6,890	115	2,680	108	3,790	104	5,420	108	6,500	109
8	3,070	127	4,370	123	5,840	114	7,200	119	2,640	109	3,800	107	5,370	105	6,520	107
9	3,060	130	4,400	124	5,830	116	7,070	117	2,600	110	3,810	107	5,470	109	6,420	106
10	3,000	124	4,340	121	5,790	116	7,090	116	2,680	111	4,020	112	5,390	108	6,640	108
11	3,340	140	4,610	127	6,130	120	7,420	125	2,910	122	4,150	114	5,480	108	6,620	111
12	3,260	132	4,560	128	5,910	122	7,290	123	2,530	103	3,920	110	5,290	109	6,460	109
13	3,280	133	4,500	124	5,870	115	7,240	119	2,770	112	3,830	105	5,350	104	6,570	108
14	2,940	123	4,330	119	5,890	117	7,230	120	2,500	105	3,910	107	5,330	106	6,300	104
15	3,000	120	4,370	118	5,610	110	7,020	113	2,550	102	3,940	107	5,120	101	6,430	104
16	3,240	136	4,570	125	6,100	121	7,120	118	2,740	115	4,100	112	5,480	109	6,590	109
17	3,150	128	4,430	125	5,900	115	7,220	119	2,520	102	3,800	107	5,280	103	6,410	106
18	3,270	131	4,500	120	5,860	112	7,050	113	2,880	116	4,050	108	5,420	104	6,470	104
19	3,280	133	4,490	124	5,990	117	7,310	121	2,710	110	3,900	107	5,400	107	6,490	107
20	3,230	138	4,620	131	6,110	122	7,470	123	2,830	121	4,110	117	5,620	113	6,930	115
21	3,200	132	4,440	125	5,830	116	7,340	121	2,780	115	4,090	115	5,550	110	6,750	111
22	2,290	99	3,300	93	4,520	91	5,550	94	1,830	79	2,750	77	3,940	79	4,740	80
23	3,200	139	4,500	129	5,950	122	7,410	123	2,540	108	3,920	109	5,180	105	6,360	105
24	3,470	163	4,580	130	6,030	121	7,490	125	3,140	136	4,010	114	5,280	106	6,470	108
25	2,940	129	4,160	118	5,420	110	6,760	115	2,140	94	3,280	93	4,460	90	5,390	92

[1] Each value is the average of five tests made on five different days. Amount of retarder used is the same amount as shown in table 4.

[2] Ratio represents the ratio (expressed in percent) of the strength of concrete with retarder to the strength of the concrete without retarder made on the same day.

4- by 16-inch beams which were used for reference purposes in volume change tests. These beams, representing mixes Nos. 1 and 2 only, had been kept continously in moist storage. When the volume change tests were completed, these beams were stored in water for 2 weeks and tested for flexural strength at an age of 15 months. The results obtained are included in table 7 and figure 8.

At an age of 15 months, the flexural strength of nonretarded concrete was the same as that of retarded concrete of reduced water content. At greater ages, the equality in flexural strength of nonretarded concrete and retarded concrete of reduced water content might be maintained.

Modulus of elasticity

The results of tests for modulus of elasticity for concretes prepared with each of the 25 retarders are not shown in this report since significant differences were not generally obtained. However, the average values recorded for all concretes are of interest. For the reference mix, the sonic modulus recorded at 7 days was 5.4 million p.s.i., and at 28 days, 5.9 million p.s.i. For mix No. 2, the sonic modulus was 5.8 million p.s.i. at 7 days and 6.2 million p.s.i. at 28 days. For mix No. 3, the sonic modulus was 5.7 million p.s.i. at 7 days and 6.1 million at 28 days.

The static modulus was somewhat lower for the three concrete mixes. At 7 days, it was 5.0 million p.s.i. for the reference mix, 5.4 million for mix No. 2, and 5.0 million for mix No. 3. At 28 days, the static moduli for the three mixes were 5.6 million p.s.i., 6.0 million, and 5.7 million, respectively.

The sonic moduli for the retarded concretes were from 3 to 6 percent higher than those for the nonretarded concrete. The static moduli of the retarded concretes were from 1 to 8 percent higher than those for the nonretarded concretes, but the average static modulus for all retarded concretes was 7 percent less than the average of the sonic values.

In general, the use of retarders did not affect adversely the modulus of elasticity of concrete unless an excessive amount of air was entrained. Retarder No. 22, which caused entrainment of an excessive amount of air, produced concrete having sonic and static moduli from 7 to 13 percent lower than those for nonretarded concrete.

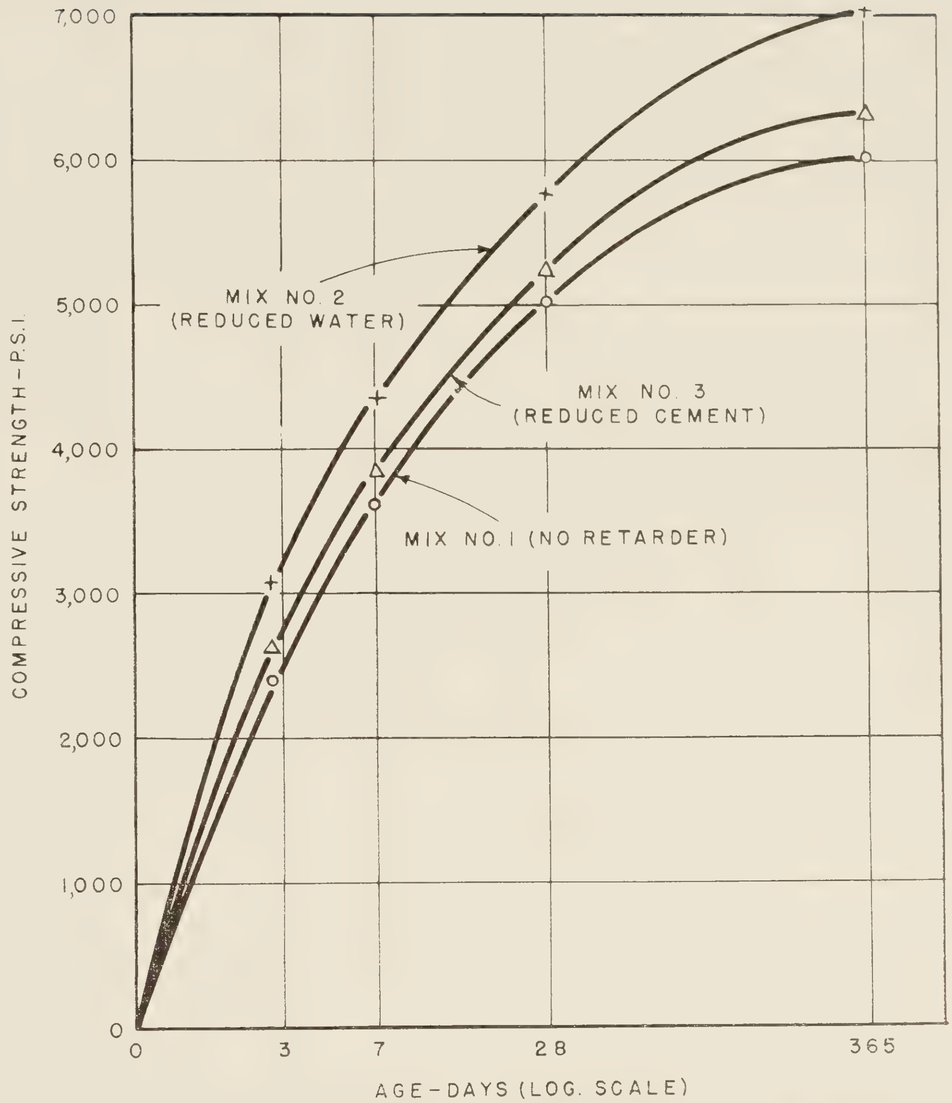

Figure 7.—The influence of retarders on compressive strength of concrete; average values for all retarders.

Effect of an elevated temperature

Tests were made to determine the effect of an elevated temperature on the properties of concrete containing each of the retarders. The materials used were stored for several days prior to mixing at 90° F. The concrete was then mixed and the test specimens were cured at the same temperature; the specimens being cured under wet burlap for 24 hours, and then stored in moist air at 73° F. until tested.

The amount of retarder necessary to give the desired retardation (2½ to 3 hours as measured by the 500 p.s.i. Proctor test) was determined and the results are given in table 8. It was found that at 90° F. more retarder per bag of cement was required for the concretes containing 19 of the retarders than for similar concretes at 73° F. With the other 6 samples (Nos. 14, 15, 16, 17, 20, and 24, all lignosulfonates) the same amount of retarder was required for both temperatures. The increase in amount used for the 19 retarders varied from 105 percent for sample No. 3, to 175 percent for sample No. 6. With respect to type of retarder, the change in temperature from 73° to 90° F. required an increase of 27 percent in the amount of the carbohydrate, and an average increase of 14 percent for lignosulfonates and 48 percent for organic acid retarders.

Retarder No. 5 caused an unusual effect on the setting or stiffening of the screened mortar at 90° F. The mortar developed a firm crust at an early age but remained soft under this crust for some time. When a Proctor penetration pressure of 500 p.s.i. was used, this crust caused the mortar to have an apparent retardation time of only 1 hour and 55 minutes. However, higher penetration pressures of over 500 p.s.i. broke through the crust and revealed the softness of the interior portion of the test specimen. Tests were continued to an age of 9 hours and the penetration pressure was less than 4,000 p.s.i. After 24 hours, the mortar was found to be hard and there was no difficulty in removing the concrete specimens prepared with this retarder from the molds. For a penetration load of 4,000 p.s.i. this retarder retarded the mortar over 4 hours. Tests of the concrete specimens at an age of 3 days indicated a satisfactory strength.

Compressive strength tests for mix No. 2 were made at ages of 3 and 28 days. The results of these tests and the ratios of these strengths to the strength of concrete without retarder, made on the same day, are shown in table 8.

In general, the same trends were shown in tests on specimens made at 90° F. as were shown on those made at 73° F. The strength ratios differed only slightly. The average compressive strength at 3 days of the concretes containing the retarders (mix No. 2) made at 90° F. was 3,020 p.s.i. and for similar concretes made at 73° F. it was 3,080 p.s.i. At 28 days, the average compressive strength of retarded concretes made at 90° F. was 5,040 and for concrete made at 73° F. it was 5,760 p.s.i.

A comparison of the compressive strengths at ages of 3 and 28 days of concrete specimens made at 90° F. and at 73° F. is shown in figure 9. At an age of 3 days, the points representing each concrete, retarded or nonretarded, are well grouped with respect to

Table 7.—Flexural strength tests [1]

Retarder No.	Modulus of rupture [2]									
	Mix No. 2						Mix No. 3			
	7 days [3]		28 days [3]		15 months [4]		7 days [3]		28 days [3]	
	P.s.i.	Ratio [2]	P.s.i.	Ratio [2]	P.s.i.	Ratio [2]	P.s.i.	Ratio [2]	P.s.i.	Ratio [2]
1	665	102	790	110	785	101	645	98	770	108
2	675	112	750	103	780	100	630	105	695	96
3	665	110	750	103	875	105	630	104	745	103
4	725	118	785	104	840	102	620	101	770	102
5	680	106	765	98	870	104	665	104	710	91
6	670	111	755	109	830	99	590	98	710	102
7	675	107	760	100	845	101	645	102	730	96
8	690	108	830	112	885	106	630	98	755	102
9	690	109	805	106	855	104	655	103	745	98
10	670	104	805	113	740	90	690	107	750	106
11	665	108	725	95	835	102	650	106	710	93
12	720	118	760	105	760	97	620	102	685	94
13	685	107	785	102	805	96	655	102	725	94
14	675	109	800	102	850	104	625	101	750	96
15	715	111	770	110	845	101	645	100	685	98
16	630	102	730	94	890	109	610	98	705	90
17	690	112	750	103	815	98	655	106	745	103
18	660	107	755	97	810	99	600	98	685	88
19	720	110	790	103	755	90	675	103	755	98
20	695	107	800	109	815	99	630	97	730	99
21	660	104	800	109	825	101	640	101	740	101
22	595	98	695	96	675	87	535	88	640	89
23	670	108	810	114	715	92	625	100	750	107
24	635	106	745	101	810	104	600	100	650	88
25	655	107	750	105	775	99	590	97	660	92

[1] Amount of retarder used is the same amount as shown in table 4.

[2] Ratio represents the ratio (expressed in percent) of the strength of concrete with retarder to the strength of the concrete without retarder made on the same day.

[3] Each value is the average of five tests made on 5 different days. Specimens were 6- x 6- x 21-inch beams tested in accordance with AASHO Method T 97 with third point loading on an 18-inch span. Side as molded in tension.

[4] Each value is the average of three tests. Specimens were 3- x 4- x 16-inch beams tested with third point loading on a 12-inch span with a 4-inch depth; bottom surface as molded in tension.

the 45° line. The concretes made with retarders Nos. 3 and 25 show the greatest reduction in strength at 3 days due to fabrication at an elevated temperature. At an age of 28 days, almost all of the concretes made at 90° F. show a lower strength. Concretes prepared with retarders Nos. 5, 7, 11, 13, 18, and 25 show this to the most marked extent. With respect to type of retarder, some differences are found but no outstanding influence of any one type is noted. Concretes prepared with retarders Nos. 3, 6, and 15, showed either none or only slight reduction in strength due to the elevated temperature.

Freezing and thawing tests

Table 9 shows the results of freezing and thawing tests made with the retarded concrete. The computed durability factors for concrete prepared with each retarder after 300 cycles of freezing and thawing are given in this table. Because of the limited capacity of the freezing and thawing apparatus the specimens for these tests were prepared on 10 mixing days.

To permit comparisons between the concretes containing the different retarders a reference mix was made on each mixing day. The specimens made with the reference mix were tested with the specimens containing the retarders, and the durability factors for each concrete of mixes Nos. 2 and 3, expressed as a percentage of the durability factor for the reference concrete made on the same day, are shown in table 9. These values are described as relative durability factors. The durability factors for the reference concrete were quite uniform, varying from 85 to 92 with an average of 90.

Concretes of equal cement content (mix No. 2) prepared with each of 3 retarders, Nos. 12, 15, and 24, had relative durabilities of 80 percent or less whereas concretes with the remaining 22 retarders had relative durabilities of 90 percent or more. Concretes of reduced cement content (mix No. 3) prepared with the same 3 retarders had relative durabilities of less than 90 percent. Concretes containing retarders Nos. 3 and 23 also had relative durabilities of less than 90 percent when the cement content was reduced.

If an assumption is made that a relative durability of 80 percent for concrete with an admixture is acceptable, as is specified in AASHO Specification M 154 for air-entraining admixtures for concrete, and in the proposed specification for retarders of Subcommittee III–h of ASTM Committee C–9, then only two retarders, Nos. 15 and 24 for mix No. 2, and three retarders, Nos. 3, 15 and 24 for mix No. 3 would not be acceptable.

Retarders Nos. 3, 15, and 24 were all of the lignosulfonate type. The air contents of the concretes containing these retarders varied from 5 to 6.5 percent and with one exception (sample No. 24 in mix No. 3) no air-entraining agent was added. Concretes containing four other lignosulfonate retarders, Nos. 20, 22, 23, and 25, to which no air-entraining agent was added to six of the eight mixes, had relative durability factors for mixes Nos. 2 and 3 varying from 86 to 103 percent. Concretes containing the other lignosulfonates to which an air-entraining agent was added, with the exception of retarder No. 12 in both mixes Nos. 2 and 3, had durability factors of over 90 percent.

Organic acid retarders Nos. 4, 5, 6, 8 and 9, which required considerable Vinsol resin solution to entrain the required amount of air in concretes for mixes Nos. 2 and 3, had relative durability factors in excess of 90 percent. Considerable amounts of air-entraining agent were also required for mixes No. 2 and 3 with

Table 8.—Retardation time for concrete and compressive strength tests of specimens made at 90° F. for mix No. 2

Retarder No.	Amount retarder used, 73° F.	Amount retarder used, 90° F.	Slump	Air	Proctor penetration test, retardation at—[1]		Compressive strength			
							3 days		28 days	
					500 p.s.i.	4,000 p.s.i.	P.s.i.	Ratio [2]	P.s.i.	Ratio [2]
	Oz./bag	*Oz./bag*	*Inches*	*Percent*	*Hr. Min.*	*Hr. Min.*				
1	1.1	1.4	3.2	4.9	3:05	2:50	2,880	121	5,090	115
2	14.4	16.3	3.2	5.8	2:45	2:10	2,550	107	4,410	99
3	4.0	4.2	3.1	5.6	2:35	2:35	3,250	132	5,260	125
4	3.0	4.2	4.4	5.5	2:20	2:15	2,890	117	5,220	119
5	4.0	6.0	4.4	5.8	[3] 1:55	4:+	3,220	135	5,080	114
6	4.0	7.0	3.6	5.8	2:45	3:35	2,770	116	5,400	122
7	3.5	4.5	3.0	5.4	2:40	2:55	2,880	117	4,700	112
8	12.0	16.0	3.3	5.1	2:35	2:50	3,210	130	5,330	121
9	2.8	4.0	2.9	6.0	3:10	3:20	3,060	124	5,220	119
10	3.2	4.3	3.2	5.2	3:10	3:00	3,090	129	5,280	119
11	4.8	6.0	2.9	5.8	2:50	2:35	3,470	140	5,070	115
12	4.0	5.3	2.7	6.9	2:35	2:55	2,840	119	5,070	114
13	4.8	5.3	2.8	5.3	3:05	2:50	2,810	114	4,540	108
14	5.0	5.0	2.7	5.6	2:20	2:30	3,180	129	5,210	119
15	4.0	4.0	3.0	4.8	2:15	2:25	3,320	134	5,470	125
16	4.8	4.8	3.0	5.3	2:20	2:00	3,350	136	5,350	122
17	3.2	3.2	2.9	5.2	3:00	2:40	2,960	120	5,270	120
18	4.0	5.0	2.9	6.5	2:25	2:40	3,060	124	4,650	111
19	4.0	4.5	2.8	5.0	2:40	2:15	3,160	128	5,390	128
20	9.0	9.0	2.9	5.4	2:30	2:25	3,030	123	5,170	123
21	9.0	12.0	2.7	5.3	2:40	2:55	3,110	130	5,420	122
22	4.0	4.5	3.5	8.+	2:25	2:45	2,340	95	3,940	94
23	6.4	7.2	3.0	5.0	2:30	2:25	3,020	126	5,100	115
24	9.6	9.6	3.0	5.4	2:40	2:30	3,580	146	5,180	123
25	4.0	5.0	2.7	7.1	2:25	2:02	2,410	101	4,280	96

[1] The delay in time of hardening of the concrete containing the retarder as compared with the concrete without retarder made on the same day. Time for concrete without retarder to reach: Proctor penetration load of 500 p.s.i.: 3 hrs. 15 min. (±15 min.); Proctor penetration load of 4,000 p.s.i.: 4 hours 45 min. (±15 min.).

[2] Ratio represents the ratio (expressed in percent) of the strength of concrete with retarder to the strength of concrete without retarder made on the same day.

[3] Top surface appeared to crust.

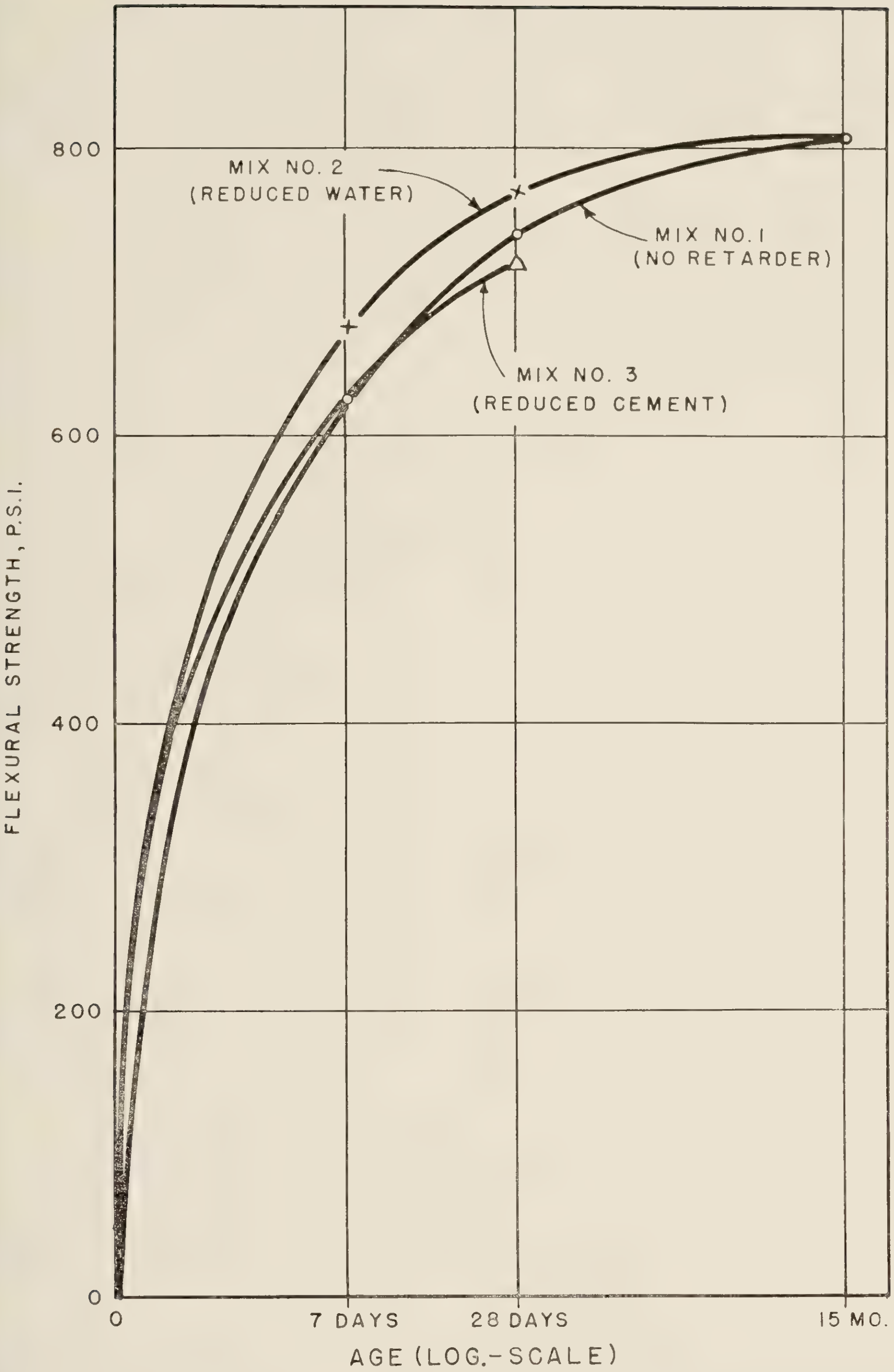

Figure 8.—The influence of retarders on flexural strength of concrete; average values for all retarders.

sample No. 1, the carbohydrate retarder. The relative durability for this concrete was 101 percent for mix No. 2 and 99 percent for mix No. 3.

Concrete having an air content of 5 to 7 percent is usually considered to have an adequate resistance to the effects of freezing and thawing. The fact that the concretes prepared with retarders Nos. 3, 15, and 24 contained at least 5 percent of air and still showed relatively poor resistance to freezing raises a question of the beneficial value of air entrained by some lignosulfonates. The only explanation which might be given to this is that the air was not in the finely divided and uniformly dispersed form most advantageous in furnishing durability to concrete. However, no study of air void size and spacing was made. The information obtained in these tests indicated that freezing and thawing tests may be of particular significance in acceptance or qualification tests of a retarder which requires no air-entraining admixture to obtain the specified air content in concrete.

Effects of delayed vibration

The results of tests to determine the effects of delayed vibration on the properties of concretes prepared with retarders are shown in table 10. During three rounds of making specimens for flexure and compression tests, an extra beam and cylinder were made for each batch. The three extra beams and three cylinders were vibrated at 3 or 5½ hours after molding. The beams and cylinders prepared with mix No. 1 were vibrated at 3 hours and those prepared with mixes Nos. 2 and 3 were vibrated at 5½ hours. The unit weight of each concrete, vibrated and nonvibrated, was determined by weighing cylinders in air and under water prior to testing at an age of 28 days.

The average increase in unit weight of all vibrated retarded concretes was 3.1 and 3.4 pounds per cubic foot for mixes Nos. 2 and 3, respectively, over the unit weights of corresponding concretes from the same batch which had not been vibrated. In general, a greater increase in weight was obtained by vibration of the concretes which had high air contents. For example, concretes of an air content of 8 or more percent (retarder No. 22) showed increases in unit weight of 6.5 and 7.4 pounds after vibration.

The average unit weights of the vibrated, reference mix prepared on 18 mixing days was 151.3 pounds per cubic foot and 148.3 pounds for the corresponding reference mix that was not vibrated. The average gain in weight of 3 pounds per cubic foot for the nonretarded mix checks with the average increase in weight of 3.1 pounds for mix No. 2 and 3.4 pounds for mix No. 3.

The average compressive strength at an age of 28 days of vibrated, nonretarded concrete (mix No. 1) was 5,680 p.s.i. This value was 11 percent higher than that for the same mix which was not vibrated. Vibration did not improve the retarded concretes to the same amount. The 28-day compressive strengths of vibrated retarded concrete were 4.1 and 7.3 percent higher, for mixes Nos. 2 and 3, respectively, than the strengths of the same concrete which was not subjected to delayed vibration. All vibrated concrete for mix No. 3 and 22 of the 25 samples tested in mix No. 2 showed a gain in strength over nonvibrated concrete.

The 28-day flexural strength of vibrated mix No. 2 averaged 2.9 percent lower than the strength of the same mix without delayed vibration. For mix No. 3 the vibrated and nonvibrated concretes had about the same flexural strength.

The average flexural strength of the vibrated, nonretarded concretes (mix No. 1) was 725 pounds per square inch. This was about one percent less than the average strength of the corresponding nonvibrated concrete.

The tests indicated that delayed vibration of retarded concrete at 5½ hours after placing was beneficial to the compressive strength. However, the time required for the 500-p.s.i. Proctor penetration pressure for delayed vibration was not applicable to concretes which were used in this study. This was probably due to the grading and the type of aggregate used.

The results of delayed vibration on flexural strength of retarded concrete included in this investigation indicate no apparent benefit, probably due to the method of vibration

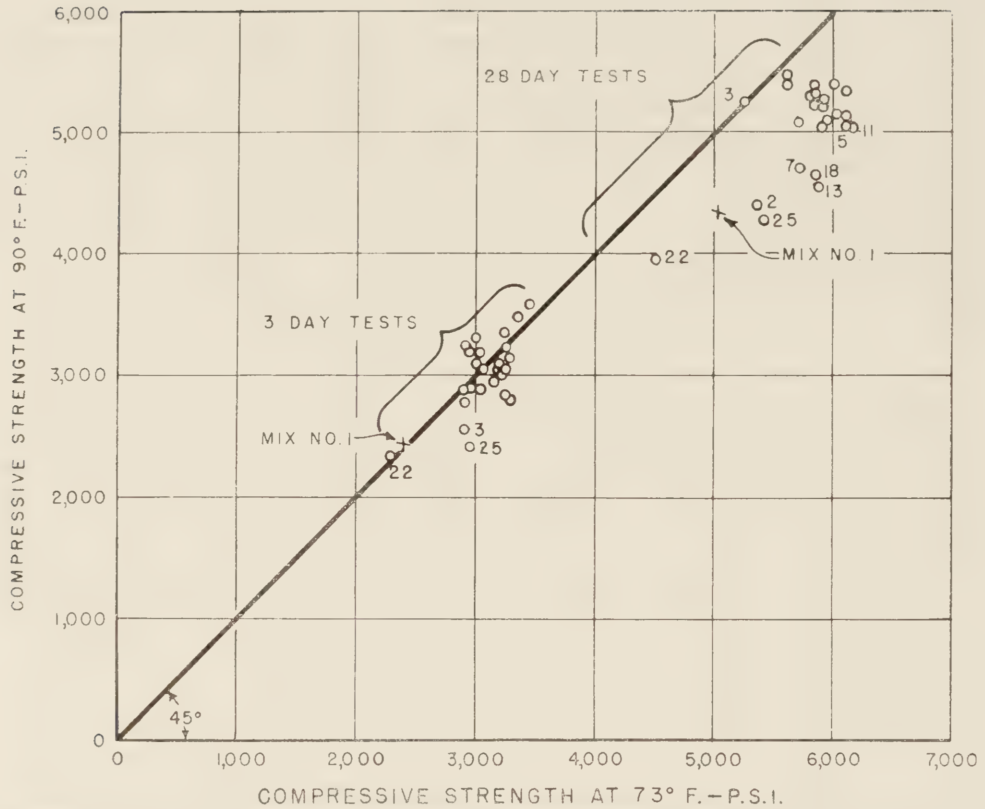

Figure 9.—Effect of elevated temperature on compressive strength of retarded concrete.

employed. It is difficult to vibrate a horizontal beam of 6- by 6-inch cross-section with a 1⅛-inch internal vibrator and obtain ideal compaction. In the case of a 6- by 12-inch cylinder, the vibrator spud is immersed for its full length in the concrete and effective vibration can be obtained.

Density and absorption tests

Data on the density and absorption of concrete disks taken from cylinders prepared with and without retarders are shown in table 11. Mix No. 2, containing each of the 25 retarders, was made on three different mixing days along with a reference mix prepared for each day. The tests were made on 1-inch thick disks which were sawed from the top, middle and bottom of three 6- by 12-inch cylinders made on the same day. Each value for weight or absorption of the hardened concrete given in the table is an average for 6 disks.

A temperature of 190° to 200° F. was used to dry the disks. This temperature was chosen because it was considered inadvisable to evaporate water above the boiling point and the uniformity of heating was better controlled at this temperature than in available ovens which operated at temperatures about 212° F.

The wet and dry densities, unit weight per cubic foot, of the disks from the bottom of the cylinders were higher than the densities of corresponding disks from the top of the cylinders. However, the differences in densities of disks from the top and middle of cylinders were relatively small and indicated very little effect on densities by any of the retarders. A comparison of densities of the retarded concretes with the densities of the reference mix also indicates a non-appreciable gain in weight above that normally obtained for the reduced water content, and the term "densifier" as used for some retarders, is not justified by these data.

The absorption data given in table 11 were calculated from the wet weights at an age of 28 days and the weights after drying at 190° to 200° F. The absorptions were higher for the disks from the top of the cylinders than for the disks from the bottom of the cylinders. There did not appear to be any appreciable effect of decreasing the absorption of the concrete in the top of a cylinder by the use of a retarder. Neither did the use of a retarder appear to decrease appreciably the range in absorption between the concrete in the top and bottom of a cylinder.

Volume change tests

The data in table 12 indicate that retarders have no significant effect on lineal drying shrinkage or growth of the concrete used in this study. This conclusion is based on a comparison of the volume change of retarded concrete with that of reference concrete which was made on the same day. In general, the organic acid retarders (Nos. 4, 5, 6, 8, and 9) and the carbohydrate retarder (No. 1) showed very little increase in shrinkage. The shrinkage values, generally, appear to be higher for the retarded concretes that were moist cured initially for 2 days than those for similar concretes that were cured initially for 14 days. Some of the lignosulfonates, particularly Nos. 11, 14, 16, 18, and 24, showed the greatest shrinkage for 2-day moist-cured concrete. Whether the calcium chloride content of retarders Nos. 11 and 24 affected shrinkage is subject to conjecture. Likewise whether reducing sugar content, over five percent in retarders Nos. 14 and 17, affected shrinkage is conjectural. Although the shrinkage values for concretes containing retarders Nos. 14 and 17 were among the highest values recorded, consideration should be given the chemical composition of each of the two retarders.

The values for expansion under moist storage showed no appreciable effect of retarders on concrete. One value, 0.019 percent, for retarder No. 14 is an exception and reference to table 1 shows that the carbohy-

Table 9.—Results of freezing and thawing tests [1]

Retarder No.	Mix No. 2				Mix No. 3			
	Air content	AEA added	Durability factor at 300 cycles	Relative durability factor [2]	Air content	AEA added	Durability factor at 300 cycles	Relative durability factor [2]
	Percent	*Ml./bag*	*Percent*	*Percent*	*Percent*	*Ml./bag*	*Percent*	*Percent*
1	4.9	16.3	92	101	5.4	21.5	91	99
2	5.2	16.3	91	100	5.6	21.5	91	99
3	6.5	------	87	96	5.6	------	68	75
4	5.2	14.3	91	101	5.1	18.0	89	99
5	5.1	10.2	87	96	4.9	13.5	82	91
6	5.3	14.3	91	100	5.4	20.2	85	94
7	6.1	10.2	90	99	5.5	13.5	87	96
8	5.0	15.1	91	99	5.3	19.3	91	106
9	4.9	14.3	94	102	5.3	18.0	87	97
10	6.0	18.4	91	99	5.7	13.5	88	97
11	5.4	4.1	88	95	5.3	9.0	84	93
12	5.7	4.1	74	80	5.9	6.7	72	85
13	5.3	4.1	88	96	6.0	6.7	79	93
14	6.0	4.1	87	94	5.3	11.2	84	99
15	6.3	------	72	79	5.0	------	64	75
16	6.2	6.1	92	101	5.5	6.7	83	98
17	5.2	10.2	92	102	5.2	13.5	86	101
18	6.2	6.1	90	99	5.0	6.7	82	93
19	5.9	8.2	91	101	5.0	11.2	87	98
20	5.1	------	85	94	5.9	13.5	91	103
21	5.0	4.1	82	91	5.2	11.2	92	103
22	10.0	------	92	101	7.9	------	91	102
23	6.1	4.1	88	97	5.0	4.7	76	86
24	5.0	------	56	61	5.9	2.4	68	76
25	7.6	------	87	96	6.6	------	87	97

[1] Each value is an average of tests on three 3- x 4- x 16-inch beams. Beams frozen and thawed in accordance with AASHO Method T 161 for fast freezing and thawing in water.

[2] Relative durability factor is the ratio in percent of the durability factor of the concrete containing the retarder to the durability factor of concrete without retarder (mix No. 1) made on the same day and given the same treatment.

drate content for this retarder is over 10 percent.

Use of excessive amount of retarder

A limited series of tests were made using four times the amount of retarder which had previously been determined as the amount necessary to obtain the desired retardation. Only ten of the 25 retarders were used in these tests which were made to determine the effect on the retardation as well as on compressive strength at ages of 7 and 28 days. The mix data for these concrete samples as well as the results of the Proctor penetration tests and the compressive strength tests and ratios, are given in table 13.

The mix data show that when four times the normal amount of retarder was used, the air content of the concrete mixtures Nos. 3, 7, and 11 was over 8 percent. No air entraining admixture was used in these mixtures. The use of an overdosage of retarder had no effect on the air content of the concretes containing each of the other seven retarders. The water required for the concretes with an overdosage of each retarder was, with one exception, reduced from that required for corresponding concretes containing the normal amount of retarder.

The time required for the concretes to reach 500 p.s.i. penetration pressure by the Proctor test, varied from approximately 6 hours for concrete containing retarder No. 11 to over 100 hours for retarders Nos. 3 and 7. For a penetration of 4,000 p.s.i., the time varied from 23 hours to over 150 hours. Retarders Nos. 11 and 12 which required approximately 6 to 10 hours, respectively, for a 500 p.s.i. penetration pressure, required 80 hours and over 150 hours, respectively, for 4,000 p.s.i. penetration pressure. Crusting of the top surface of the concrete appears to have caused this difference.

The strength tests show that at an age of 7 days, concrete prepared with retarders Nos. 1, 2, and 9 gave compressive strengths greater than those of the concrete without retarder. Concrete containing these 3 retarders reached the Proctor penetration value of 4,000 p.s.i. in less than 50 hours.

At an age of 28 days the concretes containing each of six retarders had strengths greater than the strength of the nonretarded mix. Of the four concretes which had strengths less than the reference concrete, three had air contents of over 8 percent. The concretes containing retarders Nos. 7 and 12 had strength ratios of 90–91 percent of the nonretarded concrete. As these concretes needed over 100 hours to obtain a Proctor penetration pressure of 4,000 p.s.i., it is possible that at a later age these concretes might equal the strength of the reference mix.

Where the air content of the concrete was not high, it appeared that if sufficient curing could have been given the concrete, the strength would not have been seriously lowered by the overdosage of retarder.

Figure 10 shows the probable effect of retarder overdosage on the compressive strength of concrete after 7 and 28 days. The curves showing the effect of retarders Nos. 1, 2, and 9 have approximately the same shape as that for the reference mix. The curves for the concrete retarders Nos. 3 and 11 have about the same slope as that for the reference mix. It was expected that these concretes would continue to develop strength at about the same rate as the reference concrete, and that little change in the retarded and nonretarded strength ratios would occur with increase in age.

Table 10.—Effect of delayed vibration on compressive and flexural strength of concrete at 28 days[1]

Retarder No.	Weight of hardened concrete [2]		Compressive strength, vibrated		Flexural strength, vibrated	
	Vibrated	Non-Vibrated	P.s.i.	Ratio [3]	P.s.i.	Ratio [3]
	Pounds per cu. ft.	*Pounds per cu. ft.*				
Mix No. 1	151.3	148.3	5,680	111	725	99
Mix No. 2:						
1	151.8	149.8	6,070	105	765	96
2	151.7	148.5	5,680	101	740	97
3	151.8	147.8	5,790	113	665	92
4	151.9	148.8	5,990	100	775	97
5	153.5	150.3	6,500	101	755	97
6	151.2	147.6	5,550	104	715	95
7	152.9	150.8	5,950	103	750	101
8	152.5	150.1	6,050	101	790	94
9	151.2	149.7	6,240	107	725	88
10	152.4	150.2	6,120	105	765	96
11	152.2	147.0	6,240	102	735	105
12	150.8	145.3	5,690	116	740	106
13	152.6	150.7	6,140	104	760	101
14	153.8	150.9	6,270	105	775	97
15	152.3	149.1	5,880	103	725	97
16	152.4	150.0	6,170	100	765	103
17	152.3	150.1	5,900	98	740	97
18	152.8	151.4	5,740	94	760	101
19	153.8	151.1	6,170	102	750	93
20	152.5	150.6	6,260	102	790	100
21	152.1	149.9	6,210	105	745	94
22	150.8	144.3	5,420	125	705	104
23	152.3	149.8	6,290	102	790	95
24	154.0	151.1	6,020	98	725	93
25	153.3	148.1	6,120	109	745	95
Average	152.4	149.3	--------	104	--------	97
Mix No. 3:						
1	151.6	147.6	5,810	106	695	91
2	152.0	148.4	5,360	104	730	105
3	152.2	148.6	5,610	112	710	97
4	152.0	148.7	5,560	105	725	94
5	153.5	149.8	6,270	109	705	96
6	151.1	148.9	5,320	106	675	97
7	152.2	149.8	5,830	105	735	104
8	152.4	149.7	5,690	103	725	96
9	152.4	149.3	5,910	105	755	102
10	153.2	150.7	6,000	108	720	99
11	153.6	149.7	5,710	103	685	97
12	151.7	147.8	5,360	107	745	106
13	153.8	149.6	5,890	109	720	104
14	153.0	149.3	5,610	105	740	100
15	153.5	148.8	5,950	114	670	97
16	153.2	150.0	5,690	101	735	101
17	152.1	149.4	5,790	109	750	101
18	152.6	150.5	5,600	100	760	113
19	152.8	150.1	5,790	105	735	93
20	154.0	151.0	6,380	108	680	95
21	152.5	150.5	5,800	103	720	104
22	152.4	145.0	5,190	126	670	105
23	153.0	149.9	5,580	104	765	103
24	153.6	150.7	5,600	105	670	105
25	152.6	147.6	5,880	126	670	98
Average	152.7	149.3	--------	107	--------	100

[1] Each value for mix No. 1 is average of 19 tests. Each value for mixes Nos. 2 and 3 is average of 3 tests made on different days.

[2] Weight of hardened concrete determined on test cylinders at age of 28 days.

[3] Ratio represents the ratio (expressed in percent) of the strength of vibrated concrete to the strength of the non-vibrated concrete made on the same day.

The curves for the concretes prepared with retarders Nos. 4, 5, 6, 7, and 12 show a very rapid increase in strength after a prolonged delay in hardening. The assumption drawn from the plotted data was that for these retarders a considerable delay in setting caused a very rapid gain in strength, and possibly a development of strength superior to that when normal rates of hardening occurred. This assumption, however, does not apply to all retarders which had a marked delay in setting as samples Nos. 3 and 11 had such delay but failed to gain a normal amount of strength between ages of 7 and 28 days. For most of the retarders tested, use of an excessive amount did not cause an objectionable reduction in strength at an age of 28 days.

Effect of retarders on temperature rise

Figure 11 shows the results of temperature measurements of retarded and nonretarded concretes which were stored at 73° F. for 48 hours. After mixing, retarded concretes required a longer period of time to reach the maximum temperature than did the reference mix. The increase varied from approximately

Table 11.—Density and absorption tests for mixes Nos. 1 and 2

Retarder No.	Weight plastic concrete (pounds per cubic foot)	Air in plastic concrete (percent)	Weight of hardened concrete (pounds per cubic foot)						Absorption [3] (percent)		
			Wet [1]			Dry [2]					
			Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Mix No. 1	145.7	4.5	150.8	151.6	152.0	142.6	143.6	144.1	5.8	5.6	5.5
4	145.9	4.9	151.0	150.8	152.6	143.1	142.8	145.2	5.5	5.6	5.1
9	145.3	5.1	149.5	150.2	152.5	141.2	141.9	144.8	5.9	5.8	5.3
10	144.3	5.5	149.8	150.1	152.6	141.5	142.1	145.3	5.9	5.6	5.0
11	145.9	4.7	151.9	152.6	154.2	144.1	144.6	147.0	5.4	5.5	4.9
14	145.9	4.9	152.1	152.1	153.3	144.4	144.3	146.0	5.3	5.4	5.0
16	144.3	6.5	151.0	151.0	152.7	143.6	143.3	145.8	5.2	5.4	4.7
18	145.7	5.0	151.2	151.4	154.1	143.1	143.3	146.9	5.7	5.7	4.9
20	144.3	6.0	149.5	150.1	152.4	141.2	142.2	145.0	5.9	5.6	5.1
21	144.7	5.6	150.9	151.2	152.8	143.1	143.2	145.5	5.5	5.6	5.0
Mix No. 1	144.3	5.0	149.6	149.8	151.7	141.7	141.7	144.5	5.6	5.7	5.5
3	143.1	6.5	151.6	150.3	151.8	144.3	142.6	144.7	5.1	5.4	4.9
5	145.5	5.1	152.6	151.6	153.3	145.5	144.1	146.5	4.9	5.2	4.6
6	144.7	5.2	150.1	149.7	152.0	142.3	141.8	144.8	5.5	5.6	5.0
7	144.9	5.3	151.2	150.5	152.5	143.7	142.9	145.7	5.2	5.3	4.7
8	144.1	5.5	150.3	150.1	152.0	142.5	142.3	144.9	5.5	5.5	4.9
13	143.1	6.4	149.2	149.3	151.2	141.5	141.7	144.3	5.4	5.4	4.8
15	141.9	6.7	148.8	149.0	150.9	141.1	141.4	144.2	5.5	5.4	4.6
17	144.5	5.9	151.0	150.2	152.4	143.5	142.5	145.6	5.2	5.4	4.7
19	145.5	5.0	150.9	150.6	152.5	142.9	142.6	145.3	5.6	5.6	5.0
Mix No. 1	143.5	5.0	148.3	149.1	150.6	139.5	140.5	142.7	6.3	6.1	5.5
1	144.3	5.2	149.0	149.5	151.8	140.5	141.3	144.6	6.0	5.8	5.0
2	143.9	5.2	148.2	148.4	151.1	139.7	139.9	143.4	6.1	6.1	5.4
12	144.3	5.1	151.9	151.7	152.8	144.4	144.2	145.7	5.2	5.2	4.9
22	138.6	8+	144.7	144.7	147.3	136.8	136.9	140.3	5.8	5.7	5.0
23	144.9	5.1	150.1	149.6	152.4	142.1	141.5	145.2	5.6	5.7	5.0
24	141.5	6.0	150.2	150.1	151.6	142.6	142.7	144.8	5.3	5.2	4.7
25	140.8	8+	147.8	147.9	150.0	139.8	140.0	141.9	5.7	5.6	5.7

[1] Wet weight determined on disks after 28 days continuous moist storage.
[2] Disks dried to constant weight at 190 to 200° F.
[3] Based on wet weight after 28 days moist curing.

Table 12.—Tests for change in volume for mixes Nos. 1 and 2 [1]

Retarder No.	Contraction [2]		Expansion [3]
	Moist cured 2 days	Moist cured 14 days	
	Percent	*Percent*	*Percent*
Mix No. 1	0.044	0.048	0.009
4	.046	.041	.011
9	.046	.044	.011
10	.047	.047	.013
11	.059	.048	.012
14	.052	.048	.019
16	.055	.049	.012
18	.057	.049	.008
20	.049	.046	.011
21	.047	.048	.011
Mix No. 1	.049	.046	.009
3	.049	.045	.011
5	.052	.044	.010
6	.044	.046	.011
7	.051	.047	.011
8	.044	.040	.010
13	.053	.045	.010
15	.047	.046	.012
17	.053	.056	.011
19	.052	.046	.010
Mix No. 1	.048	.044	.008
1	.046	.047	.011
2	.048	.048	.008
12	.047	.039	.009
22	.049	.044	.014
23	.052	.044	.009
24	.056	.051	.011
25	.053	.042	.011

[1] Each value is an average for three 3- x 4- x 16-inch beams.
[2] Specimens stored in dry air for 200 days at 73° F. and 50 percent relative humidity.
[3] Specimens stored in moist air for 200 days at 73° F. and 100 percent relative humidity.

one to seven hours. In only three samples were the maximum temperatures of retarded concretes higher than that of the reference mix. The greatest maximum temperature, 101° F., was found with retarder No. 24. This temperature was reached almost 7 hours after the maximum temperature of the reference concrete had been reached. The lowest maximum temperature was 90° F., obtained with retarder No. 5.

The results of measurements for temperature rise of retarded and nonretarded mortars which were screened from concrete made at 90° F. are shown in figure 12. The mortar specimens were stored in air at 90° F. for 24 hours. The increase in time for retarded mortars to reach a maximum temperature over the time required for nonretarded mortars varied from about 2½ to 16 hours. The greatest maximum temperature, 120° F., was obtained with retarder No. 24 and the lowest maximum temperature, 105° F., occurred with retarder No. 6. Somewhat of an oddity occurred with mortar containing retarder No. 5. This sample recorded the second lowest maximum temperature, 106° F., at two different times. The first temperature maximum was reached after five hours—which was prior to the time the nonretarded mortar had reached its maximum temperature—and retarder No. 5 reached 106° F. again after 23 hours.

The data show, with the single exception of No. 5 on the tests with mortar specimens, that all retarders delay the time of maximum temperature rise beyond that of nonretarded concrete and mortar. The data also show that, in general, retarders do not increase appreciably the maximum temperature rise but may decrease it. Retarder No. 24, however, presents an exception to the last statement as this sample caused both mortar and concrete to develop a significantly higher temperature than the nonretarded mixes.

Discussion of the Data

It is to be noted that the findings of this investigation apply specifically to the concrete prepared with the following materials and properties:

Cement.—Blend of four type I cements having a calculated average equivalent alkali content of 0.63 percent.

Aggregates.—Natural quartz sand, and crushed limestone of 1-inch maximum size.

Slump.—2 to 3 inches.

Air content.—5 to 6 percent.

Mixing.—In laboratory pan-type mixer.

Table 13.—Tests using four times normal amount of retarder for mixes Nos. 1 and 2 [1]

Retarder No.	Amount retarder used	AEA added	Cement	Water	Slump	Air	Proctor penetration test time for—		Compressive strength at [2]—			
							500 p.s.i.	4000 p.s.i.	7 days		28 days	
									P.s.i.	Ratio [2]	P.s.i.	Ratio [2]
	Oz./bag	*Ml./bag*	*Bags/cu. yd.*	*Gal./bag*	*Inches*	*Pct.*	*Hr. Min.*	*Hr. Min.*				
Mix No. 1	--------	27	6.0	5.9	2.7	5.4	3:50	5:25	3,650	--------	4,900	--------
1	4.5	23	6.0	5.7	2.8	5.1	20	23	4,330	119	5,500	112
2	57	17	5.9	5.8	2.9	5.1	27	29	4,160	114	5,560	113
3	16	--------	5.2	5.3	5.4	8+	100+	100+	1,480	41	2,640	54
4	12	25	6.0	5.4	3.0	5.1	80+	80+	2,380	65	5,900	120
5	16	12	6.0	5.3	4.3	4.8	15±	75	3,340	92	6,200	127
6	16	20	5.9	5.4	3.2	5.7	80+	150+	320	9	5,030	103
7	14	--------	5.8	5.2	5.2	8+	100+	150+	--------	--------	4,420	90
9	11	25	5.9	5.4	3.8	5.6	40±	48	3,860	106	5,650	115
11	19	--------	5.2	4.9	4.2	8+	6	80+	1,540	42	2,500	51
12	16	27	6.0	5.1	2.5	5.5	10±	150+	--------	--------	4,460	91

[1] Normal amount of retarder is amount required to retard the setting time of the concrete at 73° F. for 2½ hours to 3 hours.

[2] Ratio represents the ratio (expressed in percent) of the strength of concrete with retarder to the strength of the concrete without retarder.

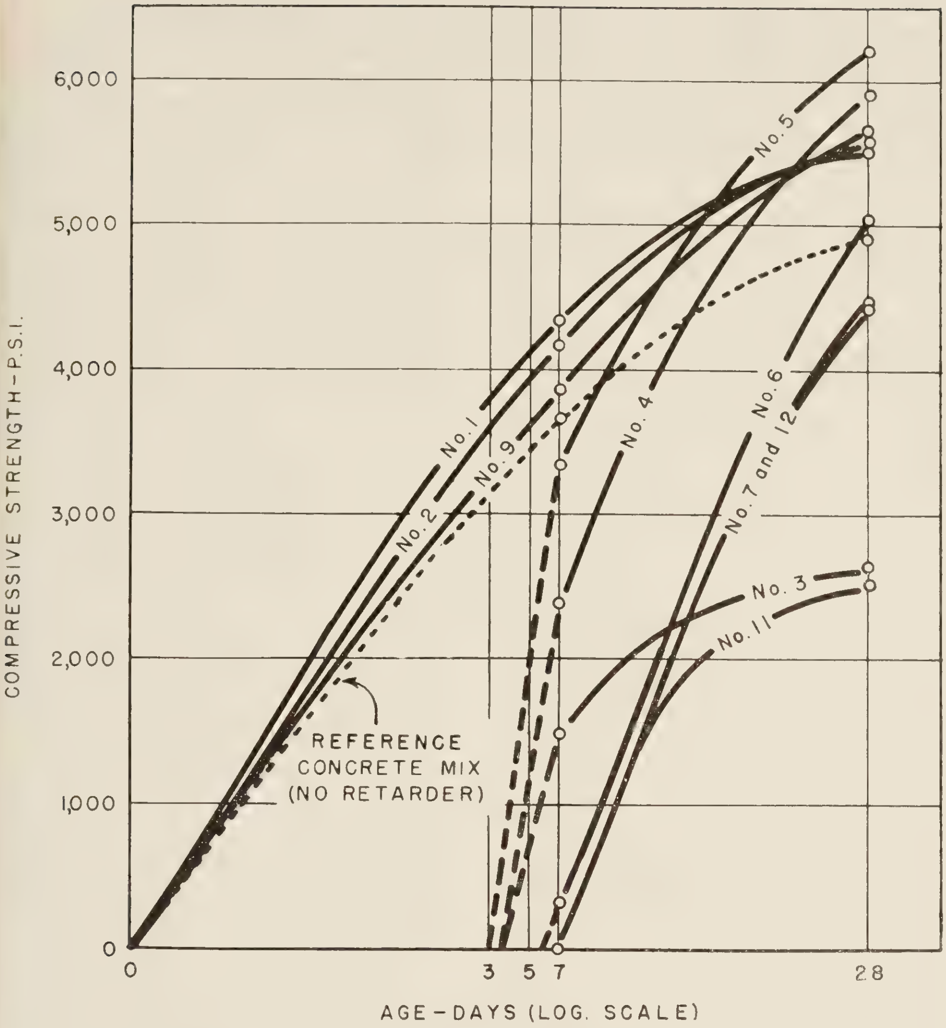

Figure 10.—Effect of overdosage (4 times) of retarder on compressive strength.

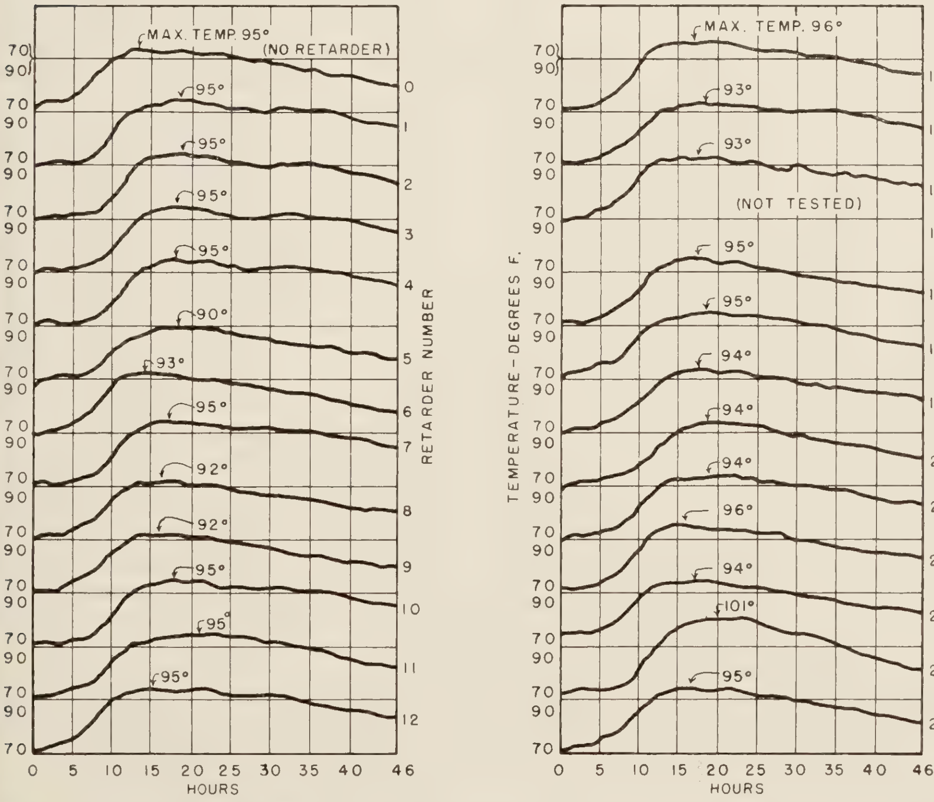

Figure 11.—Effects of retarder on temperature rise of concrete made and stored at 73° F.

When a retarder was used in sufficient amounts to delay the setting time for 2½ to 3 hours as indicated by a 500 p.s.i. Proctor penetration load, the results obtained are as follows:

- For concrete of equal cement content and equal slump, all retarders tested permitted reductions of the water content of a 6-bag concrete mix from 1 to 12 percent (0.1 to 0.7 gallon per bag of cement) below the water content of similar concrete that was not retarded.
- The chemical composition of retarders generally affected the reduction of water. The sucrose carbohydrate retarder permitted the least reduction of water, 1 percent, while the organic acid retarders permitted 5–7 percent reduction, and the lignosulfonates permitted a reduction of 5–12 percent in water content.
- The time of final hardening of retarded concretes at 4,000 p.s.i. Proctor penetration pressure was less than 11 hours; whereas the time of final hardening of retarded concretes at a pin pullout load of 8 p.s.i. was less than 10 hours.
- Concretes prepared with mix No. 2, except for retarder No. 22, had higher compressive strengths at 3, 7, 28, and 365 days than nonretarded concrete. Increases in strength at 365 days were from 9 to 25 percent. Concrete prepared with retarder No. 22, which had an air content in excess of 8 percent, had compressive strengths which were less at all ages than the strengths of the nonretarded concrete.
- Concretes which were prepared with each of 23 retarders, and which had cement contents of 5.75, 5.5, or 5.25 bags, had equal or higher compressive strengths at all ages than the reference mix with a cement content of 6 bags. Concretes containing 5.25 bags of cement which were prepared with each of two retarders had air contents of more than 8 percent and had lower compressive strengths than the 6-bag nonretarded concrete. Increases in compressive strengths of the other 23 retarded concretes were from 2 to 15 percent at an age of 365 days.
- Flexural strengths of 6-bag retarded concretes, of less than 8 percent air content, were from 2 to 18 percent higher at an age of 7 days than the reference mix flexural strength. At 28 days, the strengths of concrete containing 20 of the retarders were greater than the strengths of nonretarded concrete. The flexural strengths of the specimens which had been moist cured for 15 months were up to 9 percent greater for concretes prepared with each of 14 retarders, and from 1–10 percent lower for 10 retarders than the strengths of the reference mix. The flexural strengths at all ages for the retarded concretes containing over 8 percent entrained air were lower than the nonretarded concrete.
- Flexural strengths of concretes of reduced cement contents (5.25 to 5.75 bags per cubic yard) prepared with each of 17 retarders were, at 7 days, equal to or greater than that of the 6-bag nonretarded concrete. At 28 days, concretes prepared with each of 9 retarders showed increased strengths. When compared

with the strength of 6-bag concrete, 7 samples showed reductions of 2–3 percent at 7 days and 16 samples showed reductions of 1–12 percent in flexural strength at 28 days.

- The sonic moduli of elasticity for concretes of 6-bag retarded concrete (excluding the retarder with the high air content) were higher at 7 and 28 days than the moduli of corresponding nonretarded concrete for all but one retarder.
- The sonic moduli of elasticity for concretes of reduced cement content (5.25 to 5.75 bags) with each of 24 retarders were equal to or higher than the moduli of nonretarded concrete of 6-bag cement content except in 3 samples. Values for static modulus of elasticity, however, were generally lower than those that were determined sonically.
- In 22 cases of 6-bag retarded concrete, delayed vibration increased the compressive strengths at 28 days over that of the nonvibrated concrete. The 28-day compressive strength of retarded concrete with a content of less than 6 bags was equal to or greater than the corresponding nonvibrated concrete. The effect of delayed vibration on 28-day flexural strength was not as beneficial as on compressive strength possibly due to the method of vibration employed. Vibration increased the density of retarded concrete and a reduction of entrained air probably occurred.
- Shrinkage due to a loss of moisture was slightly greater with some retarded concretes than for the nonretarded mix. After 200 days of storage in dry air, reductions in length of 0.044 to 0.049 percent for 6-bag nonretarded concrete and 0.039 to 0.059 percent for retarded concrete were obtained. The increase in length of retarded concretes during 200 days of continuous moist storage was generally only slightly greater than that for concrete prepared without a retarder.
- Relative durability factors, the percentage ratios of the durability factor of the retarded concrete to the durability factor of nonretarded concrete, for 6-bag retarded concretes, when frozen and thawed in water, were 61, 79, and 80 with the use of 3 lignosulfonates and were 91 or greater for the other 22 retarders. Relative durability factors for retarded concrete having a cement content of 5.25 to 5.75 bags varied from 75 to 86 for 5 lignosulfonates and were 90 or greater for the other 20 retarders.
- The average absorptions at 28 days for the nonretarded mix were 5.9, 5.8, and 5.5 percent for the top, middle, and bottom sections, respectively, of a 6- by 12-inch cylinder. For retarded concretes in 6- by 12-inch cylinders, average absorptions at 28 days were 5.7, 5.5, and 5.0 percent for the top, middle, and bottom sections when an organic acid retarder was used, and were 5.5, 5.5, and 5.0 percent, respectively, when lignosulfonates were used. In general, the weight per cubic foot of the retarded concretes was only slightly higher than the weight of the corresponding nonretarded mix.

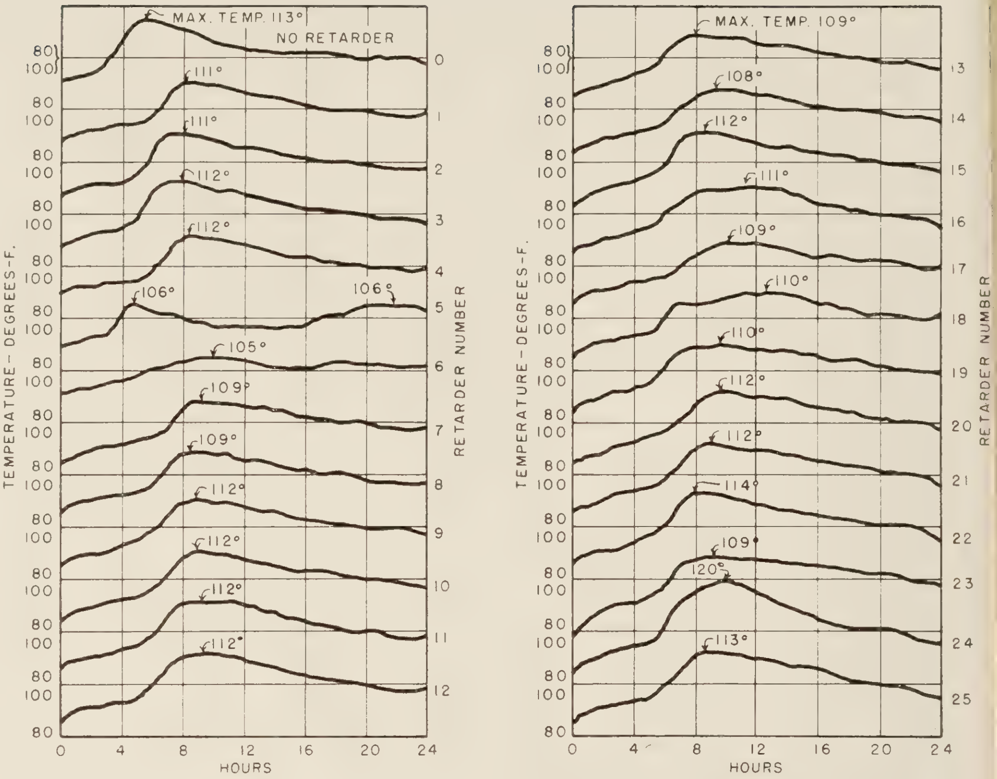

Figure 12.—Effects of retarder on temperature rise of mortar made and stored at 90° F.

- For 6 of the 19 lignosulfonates, the same amount of retarder caused a retardation of about 2½ hours (at 500 p.s.i. Proctor penetration) whether the concrete was prepared at a temperature of 73° or 90° F. For all other retarders, more material was required to retard the concrete prepared at a temperature of 90° than at a temperature of 73° F. This increase in the amount of retarder needed varied from 33 to 75 percent for the organic acids, from 5 to 37 percent for the lignosulfonates, other than the 6 mentioned above, and was 27 percent for the single carbohydrate retarder. All retarded concrete samples except one developed a final hardening (4,000 p.s.i. Proctor penetration) at a temperature of 90° F. in approximately 7 to 8 hours. Concrete prepared with the other retarder became hard at some time between 9 and 24 hours.
- Concrete prepared with 24 retarders at 90° F. (omitting retarder No. 22) had a 3-day compressive strength that was from 1 to 46 percent greater than the strength of the nonretarded mix. With the use of 2 retarders, 28-day compressive strengths of 96 and 99 percent of the strength of the reference mix were obtained but the other 22 retarders caused strength increases of from 8 to 28 percent.
- An overdosage of 4 times the normal amount of each retarder required to obtain a retardation of 2½ to 3 hours caused setting times of 23 hours to over 150 hours at a Proctor penetration pressure of 4,000 p.s.i. Of 5 lignosulfonate retarders used, 3 caused air contents of over 8 percent and the other 2 required the addition of Vinsol resin for entrainment of 5 percent air. Setting time of concrete for the overdose of the carbohydrate retarder was 23 hours at a Proctor penetration pressure of 4,000 p.s.i. Setting time of concretes (4,000 p.s.i.) with the 4 organic acid retarders varied from 48 hours to over 150 hours.

Compressive strengths at 7 and 28 days obtained for concretes with an overdosage of retarders were as follows: Three lignosulfonates (Nos. 3, 7, and 11), which entrained more than 8 percent air, were less than the strength of the reference concrete. At an age of 28 days, the reductions in strength were from 10–49 percent. Three organic acid retarders (Nos. 4, 5, and 6) were less than the strength of the reference concrete after 7 days, but were 3–27 percent higher after 28 days. A fourth organic acid retarder (No. 9) caused increases in strength of 6 percent at 7 days and 15 percent at 28 days. The carbohydrate sample (No. 1) caused increases in strength over the reference mix of 19 percent at 7 days and 12 percent at 28 days.

- Only retarder No. 24 caused concrete to have a maximum rise in temperature significantly higher than that of nonretarded concrete made and stored at 73° F. Development of the maximum temperature of the other samples tested occurred approximately 1–8 hours later than in the concrete without a retarder.

In tests of mortar specimens made and stored at a temperature of 90° F., again only retarder No. 24 caused the maximum rise in

(*Continued on page 154*)

Recommended Specification for Water-Reducing Retarders for Portland Cement Concrete

I. GENERAL

When required by specifications, or special provisions, or permitted by the engineer on written request from the contractor, an approved, set-retarding admixture that meets the requirements herein specified shall be added to the concrete.

II. ADMIXTURES

The admixture may be in liquid or powder form, and of one of the following types: [1]

A. A calcium, sodium, potassium, or ammonium salt of lignosulfonic acid.

B. A hydroxylated carboxylic acid or its salt.

C. A carbohydrate.

III. ACCEPTANCE REQUIREMENTS FOR APPROVAL OF ADMIXTURES

A. *Source of test data for approval of admixture.*—Data from a recognized laboratory that show the water-reducing retarding admixture conforms to the following requirements in this section shall be submitted. A "recognized" laboratory is any State highway, Bureau of Public Roads, or cement and concrete laboratory, inspected regularly by the Cement Reference Laboratory of the American Society for Testing Materials.

B. *Type of test data.*—The test data shall be obtained by the use of concreting materials and by methods that meet the requirements of current standards of the American Association of State Highway Officials (AASHO) or the American Society for Testing Materials (ASTM) as listed in section V of this specification.

C. *Mix requirements.*—The properties of retarded concrete prepared with the admixture under test, shall be compared with those of a reference concrete, which contains the same cement and aggregates, without retarder, and has the following composition:

Cement content—6.0±0.1 bags per cubic yard;
Air content—5.5±0.5 percent;
Slump—2½±½ inches;
Fine aggregate, by solid volume of total aggregate—36 to 41 percent.

C–1. The mixes of concrete containing the retarder shall have an air content of 5 to 7 percent, inclusive. An approved air-entraining admixture shall be used if the retarder does not entrain sufficient air.

C–2. A sufficient amount of retarding admixture shall be used to cause an increase of 50 to 60 percent in setting time over the setting time of the reference mix. The setting time for both mixes shall be determined using a Proctor penetration pressure of 500 pounds per square inch at a temperature of 73.4±3° F. for the concretes and ambient air.

D. *Required properties of retarder.*—When added to concrete in powder or liquid form, in the manner prescribed by its manufacturer or marketer and in sufficient amount to retard the setting time 50 to 60 percent, the retarding admixture shall cause the concrete to have the following properties in comparison with those of the reference concrete.

D–1. When the test and reference concrete have equal cement content and equal slump:

(a) The water content shall be decreased at least 5 percent;

(b) The air content of the retarded concrete, with or without an air-entraining admixture, shall not exceed 7 percent;

(c.1) The compressive strength at ages of 3, 7, and 28 days shall be increased at least 10 percent;

(c.2) For concrete to be used in pavement, the flexural strength shall not be reduced at an age of 7 days; at an age of 28 days, the flexural strength shall not be reduced more than 5 percent;

(d) The relative durability factor for the freezing and thawing test shall not be less than 80;

(e) The drying shrinkage at 200 days, after 2 days initial moist curing, shall not increase more than 0.01 percentage points over the shrinkage of the nonretarded concrete.

D–2. When the test concrete has a reduced cement content of ½ bag per cubic yard but the same slump as the reference concrete:

(a) The compressive strength at ages of 3, 7, and 28 days shall not be reduced;

(b) The air content of the retarded concrete, with or without an air-entraining admixture, shall not exceed 7 percent;

(c) The flexural strength shall not be reduced more than 5 percent at an age of 7 days nor more than 10 percent at an age of 28 days;

(d) The relative durability factor for the freezing and thawing test shall not be less than 80.

IV. PERFORMANCE REQUIREMENTS

When a contractor proposes to use an approved water-reducing retarding admixture he shall submit a certificate stating that the admixture is identical in composition with the sample that was used for the acceptance tests. If the admixture varies in concentration from the acceptance sample, a certificate will be required stating that the product is essentially the same for chemical constituents as the approved admixture, and that no other admixture or chemical has been added. Either prior to or at any time during construction, the engineer may require the selected admixture to be tested further to determine its effect on the strength of the concrete. When so tested, 3- and 7-day compressive strengths or 7-day flexural strengths of the concrete, made with the admixture and specified cement and aggregates, in the proportions to be used or being used on the job, shall meet the requirements of Section III D for either equal cement content or reduced cement content. A reference mix of equal or higher cement content, without the retarder, shall be made and tested with the concrete containing the retarder as a basis for comparison.

The strength relations shall be calculated on the results of at least 5 standard 6- by 12-inch cylinders or 5 standard 6- by 6- by 21-inch beams, made, cured, and tested in accordance with the current AASHO Methods T 22, T 97, and T 126, for each class of concrete at each age of test.

V. APPLICABLE SPECIFICATIONS

A. AASHO specification M 85 for portland cement, type I or II.

B. AASHO specification M 6 for fine aggregate for portland cement concrete.

C. AASHO specification M 80 for coarse aggregate for portland cement concrete.

D. AASHO specification M 154 for air-entraining admixtures for concrete.

E. AASHO method T 126 for making and curing concrete compression and flexure test specimens in the laboratory.

F. AASHO method T 119 for slump test for consistency of portland cement concrete.

G. AASHO method T 152 for air content of freshly mixed concrete by the pressure method.

H. ASTM method C 403 for rate of hardening of mortars sieved from concrete mixtures by Proctor penetration resistance needles.

I. AASHO method T 121 for weight per cubic foot, yield, and air content (gravimetric) of concrete.

J. AASHO method T 22 for compressive strength of molded concrete cylinders.

K. AASHO method T 97 for flexural strength of concrete (using simple beam with third-point loading).

L. AASHO method T 160 for volume change of cement mortar or concrete.

M. AASHO method T 161 for resistance of concrete specimens to rapid freezing and thawing in water.

N. ASTM method C 215 for fundamental transverse, longitudinal, and torsional frequencies of concrete specimens.

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[1] Other types of retarders may become available.

Water-Reducing Retarders for Concrete—Physical Tests

(*Continued from page 152*)

temperature to exceed that of mortar prepared without a retarder. Except for retarder No. 5, which developed its maximum temperature of 106° F. at two different times, the other retarders reached their maximum temperatures 3–8 hours later than did the nonretarded mortar mix.

References

(*1*) *Concrete operations in concrete ship program,* by Lewis H. Tuthill. Journal of the American Concrete Institute, vol. 17, No. 3, Jan. 1945, pp. 137–177.

(*2*) *Properties and uses of initially retarded concrete,* by Lewis H. Tuthill and William A. Cordon. Journal of the American Concrete Institute, vol. 27, No. 3, Nov. 1955, pp. 273–286.

(*3*) Discussion of a paper on *Properties and uses of initially retarded concrete.* Journal of the American Concrete Institute, vol. 28, No. 6, Dec. 1956, pp. 1187–1200.

Motor Vehicle Size and Weight Limits

A comparison of State legal limits of motor-vehicle sizes and weights with standards recommended by the American Association of State Highway Officials is given in the table on pages 140–141. The statutory limits reported in this tabulation, prepared by the Bureau of Public Roads as of July 1, 1960, have been reviewed for accuracy by the appropriate State Officials.

Statutory limits are shown for width, height, and length of vehicles; number of towed units; maximum axle loads for single and tandem axles; and maximum gross weights for single-unit truck, truck-tractor semitrailer combinations, and other combinations.

Editors note: For those who have received distribution of this table prior to this issue, please note the following corrections in footnote references: In the entries for Maryland and Ohio, the footnote numbers 31 and 44 should be deleted from the column "Axle load-pounds, Tandem, Statutory limit"; in the entry for North Dakota, footnote reference 44 should be added in the "5-axle" and "Other combination" columns under the heading "Practical maximum gross weight."

New Publications

Three new publications by the Bureau of Public Roads are now available from the Superintendent of Documents, Government Printing Office, Washington 25, D.C.

Highway Transportation Criteria in Zoning Law, dealing with the zoning law as it relates to highways is available at 35 cents a copy. This publication consists of two articles. The first article, *Highway Transportation Criteria in Zoning Law,* presents a comprehensive annotation of court decisions and statutory law dealing with the use of zoning powers to promote traffic and transportation objectives without hindering progress toward achievement of overall land-use planning goals. The article relates the extent and nature of judicial application of existing highway transportation criteria, and then suggests new criteria for consideration by the courts in handling zoning actions. Finally, the article recommends ways and means to obtain judicial acceptance of new criteria. Included is a summary of pertinent State zoning enabling legislation and a number of suggested zoning ordinance provisions.

The second article presented in this publication, *Police Power and Planning Controls for Arterial Streets,* suggests application of regulatory and zoning measures to traffic problems on urban arterial streets. A Washington, D.C., arterial street is used to illustrate the conflicting purposes and certain manifestations of deterioration sought to be remedied through the utilization of the police powers, access control provisions, and land-use and planning controls.

The second publication available which may be purchased at 20 cents a copy is a revised edition of *The Identification of Rock Types.*

In selecting the best rock for use in different types of highway construction, in planned locations of roads and bridges, and/or in locating sources of aggregates, highway engineers must be able to identify types of rocks in the field without elaborate equipment. This publication, which revises and expands the original edition of 1950, provides a simple method, suitable for field use, for the identification of the different types of rocks. *The Identification of Rock Types* will also be of great use to many other engineers, students, and other persons interested in this subject or whose work requires a limited practical knowledge of geology.

Also available is the publication entitled *Road-User and Property Taxes on Selected Motor Vehicles, 1960.* The 38-page bulletin reports the motor-fuel taxes, passenger car and truck fees, and other road-user taxes and the property taxes (where available) that would be paid on each of 13 selected typical vehicles, ranging from passenger cars to heavy truck-trailer combinations. Assuming certain conditions, such as annual miles traveled, this bulletin reports the amount of taxes paid in each State under the tax schedule in effect on January 1, 1960.

The publication has the same objectives as the three previous reports discussing taxes on selected motor vehicles, the last of which was published in Public Roads in August 1956.

The new study supplies basic data on road-user taxes as of January 1, 1960, and shows the relation of those taxes to property taxes levied on motor vehicles. A second objective of the study was to permit a comparison of the road-user taxes of each State with those of other States on similar vehicles and similar services.

Road-User and Property Taxes on Selected Motor Vehicles, 1960, may be purchased from the Superintendent of Documents, Government Printing Office, Washington 25, D.C., at 30 cents a copy.

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PUBLICATIONS
# of the Bureau of Public Roads

A list of the more important articles in Public Roads *and title sheets for volumes 24–30 are available upon request addressed to Bureau of Public Roads, Washington 25, D.C.*

The following publications are sold by the Superintendent of Documents, Government Printing Office, Washington 25, D.C. Orders should be sent direct to the Superintendent of Documents. Prepayment is required.

ANNUAL REPORTS

Annual Reports of the Bureau of Public Roads:
1951, 35 cents. 1952, 25 cents. 1955, 25 cents. 1958, 30 cents. 1959, 40 cents. (Other years are now out of print.)

REPORTS TO CONGRESS

A Report of Factors for Use in Apportioning Funds for the National System of Interstate and Defense Highways, House Document No. 300 (1958). Out of print.

Consideration for Reimbursement for Certain Highways on the Interstate System, House Document No. 301 (1958). Out of print.

Factual Discussion of Motortruck Operation, Regulation and Taxation (1951). 30 cents.

Federal Role in Highway Safety, House Document No. 93 (1959). 60 cents.

First Progress Report of the Highway Cost Allocation Study, House Document No. 106 (1957). 35 cents.

Highway Needs of the National Defense, House Document No. 249 (1949). Out of print.

Interregional Highways, House Document No. 379 (1944). Out of print.

Local Rural Road Problem (1950). Out of print.

Needs of the Highway Systems, 1955–84, House Document No. 120 (1955). Out of print.

Progress and Feasibility of Toll Roads and Their Relation to the Federal-Aid Program, House Document No. 139 (1955). Out of print.

Progress Report on the Federal-Aid Highway Program, House Document No. 74 (1959). Out of print.

Public Utility Relocation Incident to Highway Improvement, House Document No. 127 (1955). 25 cents.

Third Progress Report of the Highway Cost Allocation Study, House Document No. 91 (1959). Out of print.

PUBLICATIONS

Catalog of Highway Bridge Plans (1959). $1.00.

Classification of Motor Vehicles, 1956–57. 75 cents.

Construction of Private Driveways, No. 272 MP (1937). 15 cents.

Design Capacity Charts for Signalized Street and Highway Intersections (reprint from Public Roads, Feb. 1951). 25 cents.

Federal Laws, Regulations, and Other Material Relating to Highways (1960). $1.00.

Financing of Highways by Counties and Local Rural Governments: 1942–51. 75 cents.

General Location of the National System of Interstate Highways, Including All Additional Routes at Urban Areas Designated in September 1955. 55 cents.

Highway Bond Calculations (1936). 10 cents.

Highway Capacity Manual (1950). $1.00.

Highway Statistics (published annually since 1945):
1955, $1.00. 1956, $1.00. 1957, $1.25. 1958, $1.00.

Highway Statistics, Summary to 1955. $1.00.

Highway Transportation Criteria in Zoning Law (1960). 35 cents.

Highways of History (1939). 25 cents.

Hydraulics of Bridge Waterways (1960). 40 cents.

Legal Aspects of Controlling Highway Access (1945). 15 cents.

Manual on Uniform Traffic Control Devices for Streets and Highways (1948) (*including 1954 revisions supplement*). $1.25.
Revisions to the Manual on Uniform Traffic Control Devices for Streets and Highways (1954). *Separate,* 15 cents.

Parking Guide for Cities (1956). 55 cents.

Public Control of Highway Access and Roadside Development (1947). 35 cents.

Public Land Acquisition for Highway Purposes (1943). 10 cents.

Results of Physical Tests of Road-Building Aggregate (1953). $1.00.

Selected Bibliography on Highway Finance (1951). 60 cents.

Specifications for Aerial Surveys and Mapping by Photogrammetric Methods for Highways, 1958: a reference guide outline. 75 cents.

Standard Specifications for Construction of Roads and Bridges on Federal Highway Projects, FP-57 (1957). $2.00.

Standard Plans for Highway Bridge Superstructure (1956). $1.75.

The Identification of Rock Types (revised edition, 1960). 20 cents.

The Role of Aerial Surveys in Highway Engineering (1960). 40 cents.

Transition Curves for Highways (1940). $1.75.

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